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PAPER

Donor-(π-bridge)-azinium as D-π-A$^+$ one-dimensional and D-π-A$^+$-π-D multidimensional V-shaped chromophores†

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Heteroaromatic cations reacted with *N*-heteroarylacetylenes under Sonogashira conditions to allow easy access to potential single donor D-π-A$^+$ and V-shaped D-π-A$^+$-π-D chromophores, where the acceptor moiety A is the π-deficient pyridinium cation and the donor moiety is represented by different π-excessive *N*-heterocycles. The β hyperpolarizabilities were measured using hyper-Rayleigh scattering experiments and the experimental data are supported by a theoretical analysis that combines a variety of computational procedures, including Density Functional Theory (DFT) and correlated Hartree–Fock-based methods (RCIS(D)).

Introduction

In recent years a great deal of effort has been focused on the design and synthesis of conjugated donor–acceptor (D–A) organic molecules in the search for new materials with non-linear optical (NLO)[1] properties due to their application in opto-electronics,[2] all-optical data processing technology, biological imaging[3] and dye-sensitized solar cells,[4] *inter alia*. In this area, a number of organic compounds have been studied as possible NLO materials and it is widely accepted that active chromophores are usually composed of electron-donor and electron-acceptor moieties linked by a π-conjugated bridge, with large second-order polarizabilities related to an electronic intramolecular charge transfer effect. Chromophores of this type usually exhibit a single and intense low-lying longitudinal charge-transfer (CT) excitation and possess optical nonlinearities that are essentially dominated by a single β tensor component. However, a major problem associated with these one-dimensional (1D) dipolar chromophores is the optimization of the nonlinearity-transparency trade-off, such that the increase in the second-order hyperpolarizability β is usually accompanied by a bathochromic shift in the electronic transition.

Recently, a new synthetic strategy based on introducing multiple D and/or A substituents has been developed, including octopolar,[5] star-shaped,[6] H-shaped,[7] Λ-shaped (also called V-shaped),[8] X-shaped,[9] Y-shaped[10] and U-shaped[11] systems, with the aim of increasing the number of significant components of β. Thus, different multi-dimensional (MD) chemical systems have emerged that offer potential advantages over classical 1D linear chromophores due to the contribution of the large off-diagonal component,[12] which provides increased β responses, with the possibility of overcoming the nonlinearity-transparency trade-off.[13] Dipolar 2D NLO chromophores are primarily V-shaped (or Λ-shaped) molecules with either D–A–D or A–D–A structures. Such C_{2v} symmetric species display electronic transitions for which the direction of the transition dipole moment μ_{12} is perpendicular to the $C_2(z)$ axis, and these are associated with substantial off-diagonal tensor components β_{zyy} if the molecule lies in the *yz* plane.

In this context, organic chromophores that use charged moieties as acceptor units are restricted to diazonium salts[14] and some heteroaromatic cations such as benzothiazolium[15] and pyridinium salts,[16] which have been studied as cationic and dicationic acceptor 1D chromophores. However, very few charged 2D chromophores have been reported to date,[17] even including dipolar 2D metal-based NLO charged chromophores studied by Coe *et al.* and, more recently, a new V-shaped quinolizinium chromophore as a marker in nonlinear optical bioimaging[18] (Fig. 1) by multiphotonic interaction as TPA (two-photon absorption).

As a part of a project focused on the development of the chemistry and applications of heteroaromatic cations,[19] we considered the use of charged moieties as acceptor units in the design of NLO-active cations and the feasibility of Sonogashira[20] cross-coupling reactions as a basic strategy to obtain D-π-A$^+$ and D-π-A$^+$-π-D architectures as potentially bioactive compounds or new materials. From this perspective, our research with 1D and 2D chromophores is based on the pyridinium cation as the

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† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR for all new compounds reported and general information of OL and NLO. See DOI: 10.1039/c2ob06427h

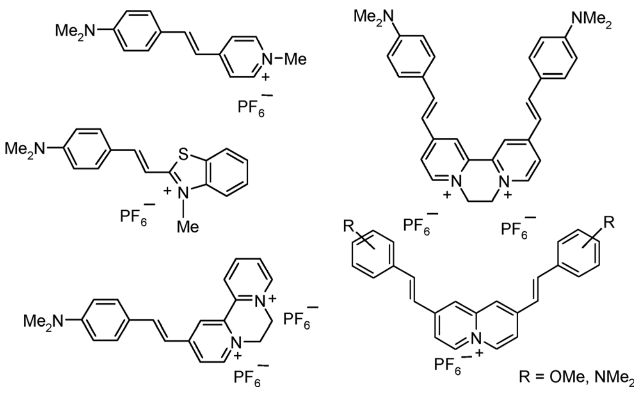


Fig. 1 Examples of 1D (D-π-A$^+$) and 2D (D-π-A$^+$-π-D) chromophores based on heteroaromatic cations as acceptor units.

acceptor unit due to the interest in organic compounds[21] that contain this unit in recent fields[22] and the use of pyridinium salts (crystals of DAST) and related species for terahertz (THz) wave generation using difference frequency mixing of two lasers.[23] These systems have potential applications in security scanning, biomedical analysis and space communication.

As a contribution to this field, and as part of our study on the chemistry of these heteroaromatic cations, their applications as molecular markers or in second harmonic generation, we report here our results on the synthesis and linear and NLO properties of both 1D and 2D charged chromophores (Fig. 2). The donor moiety is represented by π-excessive *N*-heterocycles that have different electron densities, which will, in turn, lead to larger *β* values for 2D chromophores and determine the relative magnitude between diagonal and off-diagonal *β* tensor components. Furthermore, the first hyperpolarizabilities of 1D and 2D cations were studied by hyper-Rayleigh scattering experiments and the experimental data were supported by theoretical analysis. The goal of this study was to relate the nonlinear optical responses to the molecular properties in order to gain a better understanding of molecular markers, where biological affinity and compatibility are the most critical issues for the appropriate use of NLO molecules.

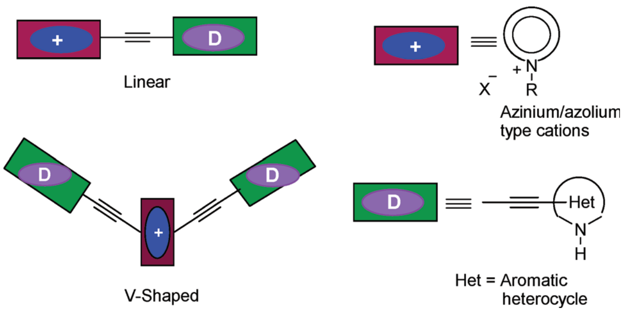


Fig. 2 Linear 1D (D-π-A$^+$) and 2D V-shaped (D-π-A$^+$-π-D) charged chromophores.

Results and discussion

Synthesis

The pyridinium system offers three possible positions to explore the scope of these charged heterocycles, because they exhibit different behaviour from an electronic point of view at the C2/C4 and C3 positions. The target 1D chromophores could be obtained by the two alternative routes shown in Fig. 3 by Sonogashira reactions. Route A would involve a Sonogashira reaction of a halo-*N*-heterocycle and an ethynylpyridinium whereas route B involves a pyridinium halide and an ethynylheterocycle.

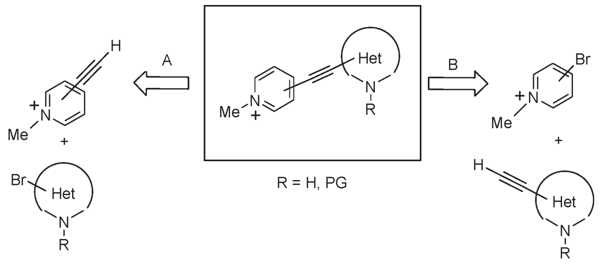


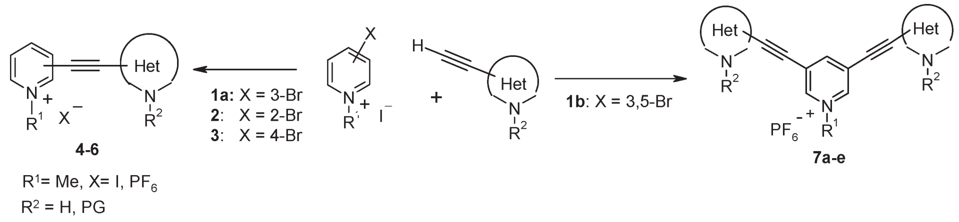
Fig. 3

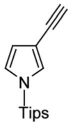
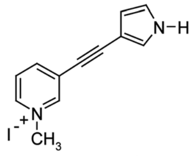
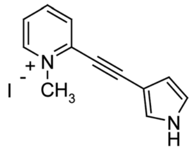
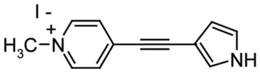
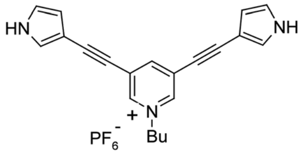
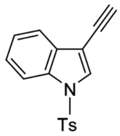
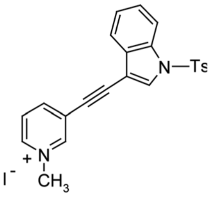
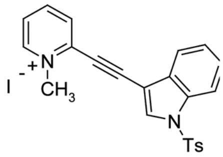
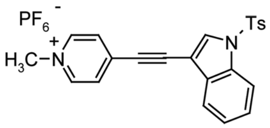
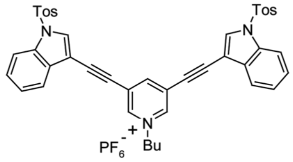
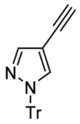
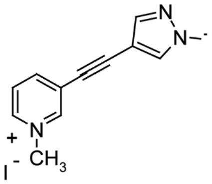
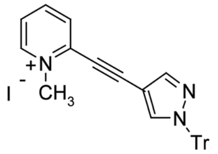
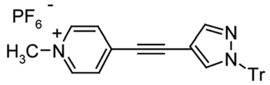
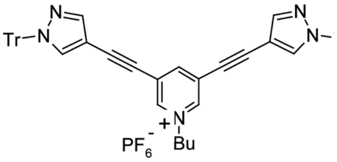
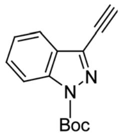
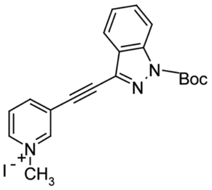
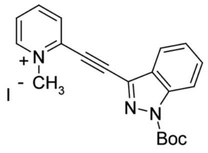
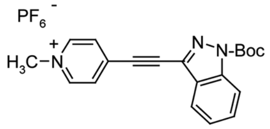
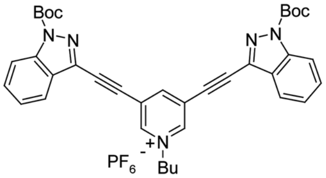
All attempts to obtain the corresponding chromophores by route A failed with pyrrole and indole heterocycles on using either the parent bromoheterocycle or the corresponding *N*-protected derivatives. Although the trimethylsilylethynyl pyridinium derivatives could be obtained in the coupling reaction between 2-, 3- and 4-brompyridinium bromides and trimethylsilylacetylene, the desilylation process could not be achieved under a variety of conditions, particularly from ethynyl derivatives at the C3- and C4-positions. Consequently, we focused our attention on the coupling of the corresponding bromopyridinium salt (**1**–**3**) with heteroaryl-acetylenes (route B).

Initially, considering the conditions recently described by us,[18] the cross-coupling reaction of 3-bromopyridinium bromide (**1a**) with protected *N*-heteroaryl acetylenes[24] was carried out in the presence of 10 mol% of copper(I) iodide, 5 mol% $PdCl_2(PPh_3)_2$ and 1.5 equiv. of Et_3N in DMF, with the reaction mixture stirred for 8 h at room temperature. Under these conditions coupling of **1a** with pyrazole and indazole gave **4c** and **4d** in 48% and 57% yields, respectively (Table 1, entries 3 and 4). The same yields could also be obtained by heating the mixtures at 65 °C for 4 h (Method A). However, under the same conditions the preparation of derivatives **4a** and **4b** from pyrrole and indole was unsuccessful, giving rise the homocoupling product of the corresponding ethynyl acetylene and the dehalogenated *N*-methyl pyridinium iodide. The homocoupling reaction with pyrrole and indole derivatives was avoided by adding 10 mol% of LiCl[25] in the presence of the same catalytic system [$PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%)] and Et_3N in DMF. Under these conditions the expected coupling compounds **4a** and **4b** were obtained at room temperature after 20 h (Method B) in 63% and 61% yields, respectively. As was the case for **4c**,**d**, heating at 65 °C reduced the reaction time without affecting yields. It is noteworthy that deprotection (TIPS) of the pyrrole ring in isolated compound **4a** was observed, but all attempts to deprotect isolated compounds **4b**–**d** were unsuccessful, with extensive recovery of the protected compounds under acidic conditions and decomposition under basic conditions. Furthermore, the attempted formation of a heterobetainic structure for chromophore **4a** under basic conditions resulted in decomposition.

We next examined the coupling at the C-2 and C-4 positions of the pyridinium ring. On examining the two methods (Method

Table 1 Synthesis of chromophores **4–7** by Sonogashira reaction on bromo pyridinium salts



Entry	Acetylene	Coupling Product (**4-7**) Yield (%)			
1		 **4a** (63)[b]	 **5a** (26)[b]	 **6a** (32)[b]	 **7a** (55)[c]
2		 **4b** (61)[b]	 **5b** (70)[b]	 **6b** (50)[b]	 **7b** (83)[c]
3		 **4c** (48)[a]	 **5c**(45)[a]	 **6c** (77)[a]	 **7c** (80)[c]
4		 **4d** (57)[a]	 **5d** (53)[a]	 **6d** (69)[a]	 **7d** (80)[c]

[a] **Method A**: $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), DMF, Et_3N, 65 °C [b] **Method B**: $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), LiCl (10 mol%) DMF, Et_3N, r.t. [c] **Method C**: $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), THF, Et_3N, r.t.

A or B) for the coupling on 1D, it was found that method A was efficient with pyrazole and indazole at the C2/C4 positions and Method B for pyrrole and indole, with moderate to good yields obtained at room temperature for compounds **5a–d** and **6a–d** (see Table 1). Regarding the reactivity of the different halogenated positions in the pyridinium ring and the yield of the coupling product, the electronic character of the less activated position at C3 did not have a significant effect on the yield. However, in 2- and 4-bromopyridinium the different yields obtained could be related not only with the activation of α and γ positions but also with the instability of the alkyne.

The use of a double substitution strategy enabled the synthesis of different V-shaped molecules with the aim of understanding the NLO properties of charged chromophores by hyper-Rayleigh scattering experiments.[26] Initially, chromophores **7** (D-π-A^{+}-π-D) were synthesized from 3,5-dibromo-1-methylpyridinium iodide by a double Sonogashira reaction, under the optimized conditions found for monoderivatives 1D, with a change in the corresponding equivalents of alkyne (2.4 equiv) and the base (3 equiv). However, yields of the coupling products were low, mainly due to problems encountered in the work-up and purification of the products. To overcome these problems, the PF_6 salt[27] of 3,5-dibromo-1-butylpyridinium was employed instead of the corresponding methylpyridinium derivative. This salt has the advantage of solubility in THF, thus facilitating the work-up. In this way, compound **1b** was reacted with different heteroarylacetylenes to afford the corresponding coupling products **7a–d** as hexafluorophosphates under Sonogashira conditions (Method C) similar to those used for compounds **4–6**. The results are summarized in Table 1. Compounds **7b–d** were obtained in good yields but only a moderate yield was achieved for **7a**, which was also isolated with both pyrrole rings deprotected.

Linear optical properties

Absorption spectra of the 1D (**4–6**) and 2D V-shaped (**7**) compounds were monitored in the 230–800 nm range. The absorption spectra for these compounds are shown in Fig. 4 and did not exhibit significant absorption above 450 nm. The relatively intense peak at the longest wavelengths is ascribed to the π–π* intramolecular charge transfer (ITC) absorption band from the pyridinium acceptor moiety. The positioning of the maxima for these bands is usually rather sensitive to the degree of conjugation and to the electron-donating characteristics of the substituent. Most of the chromophores, with the exception of **4a**, **4c**, **6d** and **7b**, which exhibit a weak overlapping band, show a sharp cut-off for the π–π* transition band. The overlapping band, which is observed at a longer wavelength relative to the maximum for the π–π* band, may be ascribed to the n–π* transition due to the presence of N heteroatoms and the triple bond. These bands are characterized by molar absorptivities that are usually somewhat smaller than those for π–π* transitions.

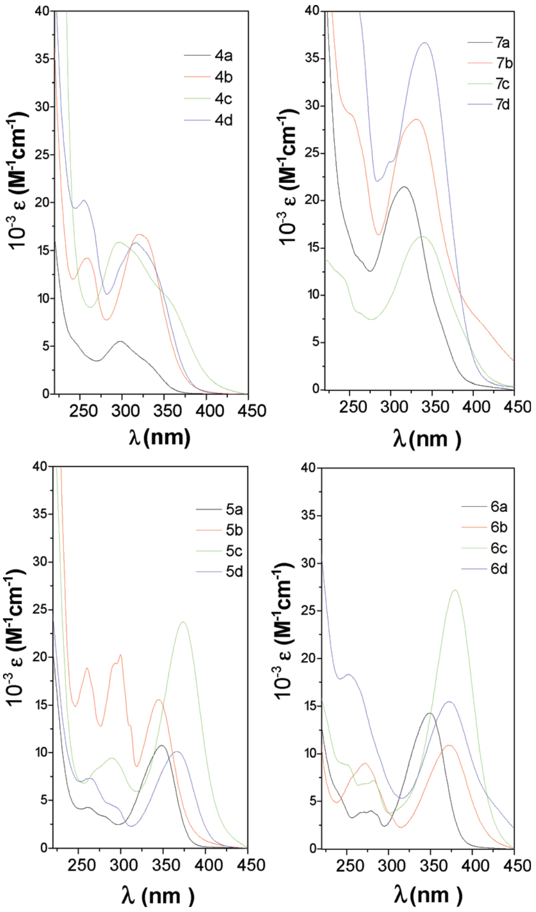
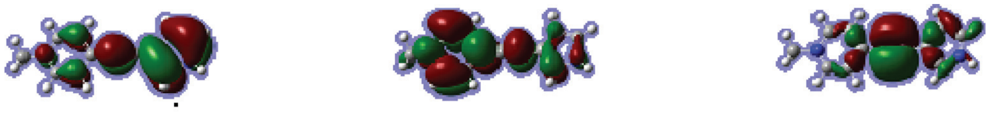


Fig. 4 Absorption spectra for compounds **4–7** in methanol at 25 °C.

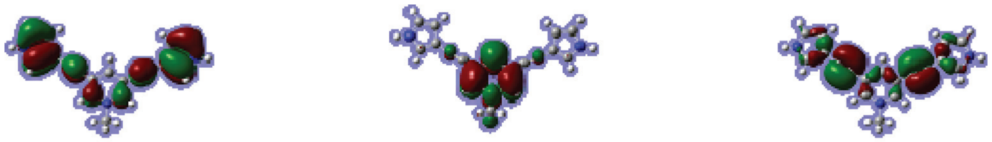
The molecular orbitals involved in these transitions for **6a** and **7a** are shown in Fig. 5 and 6 and were calculated at the HF/6-31G(d) level of theory. These MOs represent the main component of the π–π* band due to a HOMO–LUMO transition and the in-plane n–π* triple bond molecular orbitals involved in the transitions between HOMO-2 and LUMO and HOMO-4 and LUMO band rather than the in-plane heteroatom lone pairs.

In general, little correlation was found between the electron donating characteristics of the different pyrrole (**a**), indole (**b**), pyrazole (**c**) and indazole (**d**) substituents of the pyridinium acceptor and the location of the wavelength for the π–π* ITC absorption band for all the different systems. Compounds **4**,



HOMO = (-10.87 eV)   LUMO = (-2.54 eV)   HOMO-2 = (-13.98 eV)

Fig. 5 HOMO, LUMO and HOMO-2 for compound **6a** at the HF/6-31G(d) level of theory.



HOMO = (-10,40 eV)   LUMO = (-1,95 eV)   HOMO-4 = (-13,49 eV)

Fig. 6 HOMO, LUMO and HOMO-4 for compound **7a** at the HF/6-31G(d) level of theory.

Table 2 Linear optical data for **4–7**

Compound	λ_{max}	λ_{exc}	λ_{em}	ε ($M^{-1}cm^{-1}$)	Φ_f ($\times 10^2$)	$<\tau>$, ns
4a	297	310	434	5500	8.9	1.1
4b	319	—	—	16 700	—	—
4c	293	—	—	15 750	—	—
4d	317	—	—	15 800	—	—
5a	348	370	526	10 750	0.04	1.0
5b	345	345	537	15 600	0.9	0.7
5c	374	350	495	23 700	9.0	2.5
5d	366	345	492	10 100	3.0	2.0
6a	348	—	—	14 300	—	—
6b	372	370	459	10 900	0.25	2.7
6c	380	—	—	27 200	—	—
6d	372	365	495	15 450	0.8	1.0
7a	317	—	—	21 450	—	—
7b	332	—	—	28 600	—	—
7c	338	330	494	16 250	17.0	2.3
7d	341	325	496	36 700	30.4	2.0

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 compounds **4** and **7** in methanol at 25 °C.

where donors are substituted at the C3(*β*) (*meta* substitution) and the conjugation is less efficient, is the only compound which follows the expected trend. For the latter compounds the pyrazole substituent, which is the weakest donor, yields the shortest λ_{max} for the π–π* transition. The indole and indazole are the best donors and yield the highest λ_{max}. Wavelengths for the absorption maxima (λ_{max}) of the π–π* band are collected in Table 2 along with the molar absorptivities (ε) at these wavelengths.

Greater influence of the position of the donor substituent at the pyridinium acceptor on the placement of the absorption bands, however, were observed. A substituent at the C4(*γ*) position of the pyridinium resulted in the most efficient conjugation, while the one at C3(*β*) was the least efficient. The effect at the C2(*α*) position is usually somewhere between both due to electronic and steric effects. Therefore longer wavelengths for the absorption maximum are detected for compounds **6**, and **5** ($\lambda_{max,6} \geq \lambda_{max,5}$) in comparison with **4**. Thus, the λ_{max} values for **5a**, **d** and **6a**, **d** are ~50 nm higher than those for **4a**, **d**. These differences are, however, larger than 80 nm when comparing compounds that contain the weakest donor pyrazole substituent, *i.e.* **5c** and **6c** with **4c**.

The addition to 1D compounds named **4** of a second heterocyclic donor group linked to the pyridinium acceptor moiety at C(5) by a triple bond to give 2D V-shaped **7** compounds, contributes to extending the π-delocalization and ICT stabilization. The effect on λ_{max} for these V-shaped compounds can be seen as the balance of a *meta* substitution that provides a less effective conjugation and di-substitution which contributes to extend it. As a results, an intermediate effect on λ_{max} between compounds **4** and **5** or **6** was obtained for **7**. This situation is consequently reflected in a bathochromic displacement of the π–π* band by about 13–45 nm for compounds **7** relative to compounds **4**. Nevertheless, this stabilization does not permit reaching the absorption wavelengths for **5** and **6**. It is also remarkable that molar absorptivities at λ_{max} are significantly higher for V-shaped compounds **7** (15 000–37 000 $M^{-1}cm^{-1}$ range) than for **4** (5500–16 700 $M^{-1}cm^{-1}$ range) and other 1D (**5**, **6**) systems.

Fluorescence data, obtained from the analysis of the emission spectra in the 350–700 nm range upon excitation of the π–π* band at the λ_{exc}, are also collected in Table 2. All spectra – with the exception of those for compounds **4b–d**, **6a**,**c** and **7a**,**b**, which did not fluoresce – exhibit single bands, the maxima (λ_{em}) of which depend on the nature of the compound. However, among the fluorescent systems, discrete correlations between λ_{em} and the electron-donating characteristics of the substituent (**5a–d**) and/or its position at the pyridinium acceptor (**5d**, **6d** and **7d**) were observed.

Something similar occurs for fluorescence quantum yields and lifetimes. In general, 1D systems exhibit zero or very low fluorescence quantum yields. 2D systems **7c**,**d** are the only ones that have a noticeable fluorescence. Low fluorescence in polar solvents is usually attributed to the stabilization of the ICT excited state and thus increases the probability of deactivations through other non-radiative pathways.[28] All the fluorescence intensity profiles for the fluorescent samples, measured at λ_{em} upon λ_{exc}, were fitted to bi-exponential decays This denotes the involvement of some processes other than the simple radiative emission from a singlet to the ground state. As stated before, it is quite difficult to assign any correlation between the quantitative values for Φ_f and lifetime averages ($<\tau>$), collected in Table 2, and the electron-donating character, the location of the substituent or the number of substituents for these systems where several complex deactivation excited state processes were involved. The low fluorescence quantum yields and subsequently the uncertainty in both Φ_f and $<\tau>$ measurements also contribute to this.

Nonlinear optical properties: Hyper-Rayleigh Scattering (HRS) measurements and computational details

Femtosecond hyper-Rayleigh scattering measurements performed at 800 nm for all compounds presented in Table 3 confirm the potential of these small ionic compounds for second-order nonlinear optics. The second-order nonlinear optical properties reflect the observations already made in linear optics in terms of the nature of the conjugation. According to the

Table 3 Experimental nonlinear optical properties of 1D and 2D chromophores

Compound	$\lambda_{\max}$	β_{HRS}	β_{zzz}	$\beta_{zzz,\,0}$	τ
4a	297	42± 3	103 ± 7	32 ± 2	1.4 ± 0.4
4b	319	25 ± 3	60 ± 8	18 ± 2	—
4c	293	18 ± 2	44 ± 6	17 ± 2	2.7 ± 1.3
4d	317	13 ± 7	32 ± 18	9 ± 5	0.3 ± 0.2
4e	292	16 ± 6	40 ± 16	16 ± 6	—
5b	345	110 ± 14	267 ± 35	32 ± 4	—
5c	374	61 ± 3	148 ± 6	29 ± 2	1.0 ± 0.3
5d	366	16 ± 9	39 ± 22	8 ± 4	—
5e	346	37 ± 4	90 ± 9	18 ± 2	—
6a	348	112 ± 16	270 ± 40	64 ± 9	—
6b	372	113 ± 13	274 ± 32	31 ± 3	—
6c	380	NLR			
6d	372	125 ± 20	303 ± 49	32 ± 5	—
6e	360	67 ± 6	163 ± 16	27 ± 3	—
7a	317	NLR			
7b	332	NLR			
7d	341	68 ± 21	164 ± 51	64 ± 14	1.5 ± 0.6

NLR: non-linear relation. Wavelength of maximum absorption $\lambda_{\max}$ (nm), resonant 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.

Table 4 Theoretical values for the optical properties of 1D and 2D chromophores. Wavelength of maximum absorption $\lambda_{\max}$ (nm), HRS first hyperpolarizability at 800 nm $\beta_{HRS,800}$, diagonal averaged first hyperpolarizability at 800 nm $\beta_{zzz,800}$, depolarization ratio at 800 nm ρ_{800}, off-resonance components of the molecular first hyperpolarizability β_{zzz} and β_{zxx} (10^{-30} esu), dipole moment in Debye and the reduced vector component of molecular first hyperpolarizability β_z (10^{-30} esu)

Comp.	$\lambda_{\max}$ CIS(D)	$\beta_{HRS,800}$	$\beta_{ZZZ,\,800}$	ρ_{800}	$\beta_{zzz,0}$	$\beta_{zxx,0}$	μ_z	β_z
4a	317	46	42	5.2	−51	−1	−3.1	−66
5a	323	61	55	4.9	59	0	1.7	88
6a	354	115	105	4.8	99	−1	2.9	165
7a	327	47	40	2.8	5	39	3.8	51
5d	314	69	63	4.9	65	3	6.7	99
4d	287	44	40	5.1	47	2	8.4	62
6d	344	119	109	4.8	−107	2	−8.3	−171
7d	306	49	42	2.7	3	45	4.4	57

trends already observed in the linear optical (absorption) experiments, the largest first hyperpolarizability values were found for some indole (**5b**: $\beta = 110 \times 10^{-30}$ esu, **6b**: 113×10^{-30} esu) and indazole (**6d**: $\beta = 125 \times 10^{-30}$ esu) derivatives, but also for pyrrole (**6a**: $\beta = 112 \times 10^{-30}$ esu). In agreement with the greater influence of the position of the donor substituent at the pyridinium acceptor – more than their relative electron donating strength characteristics – and the better conjugation and stabilization, the largest β values correspond to the compounds whose substituents are at the C4(γ) and C2(α) positions on the pyridinium system, confirming that the best conjugation and charge transfer from donor to acceptor is achieved in these positions. The subtle differences between C2(α) and the C4(γ) positions are attributed to steric effects, leading to shorter wavelength of maximum absorption and smaller hyperpolarizabilities for C2(α) if differences are observed, pointing to torsional angle effects in the *ortho* position. In general, no fluorescence is observed at the second harmonic wavelength for these compounds with red-shifted absorption and fluorescence, with respect to the C3(β) or *meta* substitution.

For the V-shaped compounds **7**, we see the combined effect of the inefficient *meta* substitution with the extended conjugation along the two arms resulting in intermediate properties, both for the wavelength of maximal absorption and for the hyperpolarizability. Also in agreement with the observation for compounds **4**, C3(β) substitution, we observe again two-photon fluorescence, and correct for this contribution with the fluorescence lifetime indicated in Table 3.

The theoretically calculated β_{HRS} (see Table 4) also follow the same behaviour and the agreement between experimental and theoretical β_{HRS} values for compounds **6a** and **6d** warrants particular mention. Furthermore, the 2D or V-shaped D-π-A^{+}-π-D chromophores, in comparison with the 1D D-π-A^{+} chromophores, have a higher nonlinear response (*cf.* **7d** and **4d**) in accordance with the progression in absorption maxima to higher wavelengths and the increase in the molar adsorptivities.

According to the HRS theory (see eqn (1), (2) and (3) in the ESI†), for a typical experiment a clear linear dependence of the HRS response QC (quadratic coefficient) is observed as a function of concentration and the ratio of the slopes is directly proportional to the ratio of their orientationally averaged hyperpolarizabilities squared. However, for compounds **6c**, **7a**, **7b** and **7c** the data obtained for the samples were plotted, with the Y-axis representing the quadratic coefficient QC of the HRS signal and the X-axis the concentration of the sample. A linear fitting was not obtained and the data could not be used to calculate any hyperpolarizability (see ESI†).

On the other hand, because of the two-photon resonance enhancement that varies with the wavelength of the charge transfer, all of which are relatively close to the second-harmonic wavelength, the dynamic values for the first hyperpolarizability measured at 800 nm are not directly comparable. Taking into account this resonance enhancement by using the simple two-level formalism REF, it is possible to compare values for the static first hyperpolarizability, β_{o}. These values are the most relevant ones for comparison. It is clear that the largest, corrected nonlinearities are found for the better C4 substituents or for the V-shaped compounds **7d**.

Theoretical calculations were performed using the Gaussian suite of quantum chemical programs.[29] For all the studied cationic chemical systems, the molecular structures used to compute optical properties correspond to energy minima calculated at the HF/6-31G(d) level of theory. These structures were confirmed to be minima by evaluation of the harmonic vibrational frequencies, which all proved to have real values. Calculated wavelengths ($\lambda_{\max}$, in nm) were estimated from CIS(D)[30] and DFT methods and theoretically predicted values of the second harmonic generation (SHG) of hyperpolarizability $\beta(2\omega;\omega,\omega)$ was obtained including the electron correlation effect by the MP2/6-31G(d) level. This property $\beta_{MP2}(-2\omega;\omega,\omega)$ was estimated from the resonant or dynamic $\beta(-2\omega;\omega,\omega)$ at the HF/6-31G(d) level, and the static or non-resonant $\beta(0;0,0)$ was calculated at both HF/6-31G(d) and MP2/6-31G(d) levels following the multiplicative approximation scheme, where the frequency dispersion is estimated to be similar at these two levels of theory.[31] No solvent effects were considered in our quantum chemical calculations.

$$\beta_{MP2}(-2\omega;\omega,\omega) \approx \beta_{HF}(-2\omega;\omega,\omega)\frac{\beta_{MP2}(0;0,0)}{\beta_{HF}(0;0,0)} \qquad (1)$$

The Hartree–Fock (HF) values were calculated analytically and the MP2 values were obtained numerically. The calculated hyperpolarizability tensor elements are given in the molecular axes basis β_{ijk} and these must be transformed to the laboratory axes β_{XYZ} by applying the expressions of Civin *et al.*[32] The theoretical β_{ZZZ} values are lower than the β_{HRS} values since the former values are only part of the latter. However, in the experimental determination of the β_{ZZZ} values the old two states model approximation is applied. The molecular hyperpolarizability tensors $\boldsymbol{\beta_{ijk}}$ can be reduced to vector components $\boldsymbol{\beta_i}$ (eqn (2) depolarization ratio ρ (eqn (3)) and β_{HRS} (eqn (4)) are given by:

$$\beta_i = \sum_{j-x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad (2)$$

$$\rho = \frac{\langle \beta^2_{ZZZ} \rangle}{\langle \beta^2_{XZZ} \rangle} \qquad (3)$$

$$\beta_{HRS} = \sqrt{\langle \beta^2_{ZZZ} \rangle + \langle \beta^2_{XZZ} \rangle} \qquad (4)$$

All theoretical data calculated for selected compounds are shown in Table 4. The data in this table include the theoretically predicted λ_{max} values for the first excited electronic state. The calculated wavelengths for compounds containing pyrrole groups as donors (**4a–7a**) show positive and negative deviations from the experimental values by less than 7%, whereas for the compounds containing indazole groups the calculations underestimate the experimental values, with deviations in the range 8–14%. The estimated β_{HRS} also follows a similar trend and depolarization ratio at 800 nm, ρ_{800} take values close to 5 or 3 as it should be for linear and dipol chromophores, respectively.

For all these systems the β_{HRS} is given mainly by the spatially averaged β_{ZZZ}. In contrast, for the 1D and 2D systems only the diagonal β_{zzz} and off-diagonal β_{zxx} elements of the molecular first hyperpolarizability tensor are meaningful, respectively.

When the molecular hyperpolarizability is reduced to a vector according to eqn (2), only the parallel component β_z is presented either for 1D or 2D systems because this has values that are 10 times larger than those of the orthogonal β_x or β_y. The angles between dipole moments and the reduced first hyperpolarizability vectors are 0.4° and 0.7° for **7a** and **7d**, respectively, showing that both are parallel in these 2D or dipolar chromophores. In contrast, for the 1D or linear chromophores this angle ranges from 10° to 30°, being 11° and 12° for **6a** and **6d**, respectively, and 30° for **5a**.

Conclusions

The C_{2v} symmetric 2D (D-π-A$^+$-π-D) systems and their 1D (D-π-A$^+$) analogues were synthesized in moderate to good yields by Sonogashira cross-coupling reactions from bromopyridinium salts and ethynylheterocycles. The first hyperpolarizabilities of the series of charged chromophores (D-π-A$^+$) and (D-π-A$^+$-π-D) were determined by HRS. The results show that a large first hyperpolarizability was obtained in compounds **5b**, **6a**, **6b** and **6d**. The low transition energy and high level of CT are the decisive factors that give a large first hyperpolarizability in compounds substituted at C4. Theoretical calculations support the experimental results obtained.

The synthesis and study of these new compounds are allowing us to deduce valuable structure–activity relationships for use in ongoing studies focused on the optimization of 2D-TPA and applications in bioimaging.

Experimental

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

Method A (4, 5, 6c–d). A flame-dried flask was charged under argon with 1 equiv. of bromopyridinium iodide or hexaflourophosphate, 10 mol% CuI (0.0667 mmol, 0.0127 g) and 5 mol% $PdCl_2(PPh_3)_2$ (0.0333 mmol, 0.0234 g) in dry DMF (10 mL). 1.2 equiv. of the corresponding acetylene heterocycle (0.7551 mmol) and 1.5 equiv. of Et_3N (0.9438 mmol, 0.1315 mL) were added. The mixture was heated at 65 °C for 4 h and the solution was filtered through a small pad of celite and washed with methanol. The solution was concentrated, treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the solid was purified by flash chromatography on silica gel in CH_2Cl_2/MeOH (9.5 : 0.5) as eluent.

*1-Methyl-3-(1-trityl-1*H*-pyrazol-4-ylethynyl) pyridinium iodide (4c).* Following the general procedure A, from **1a** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), afforded 0.1812 g (48%) of **4c** as a yellow solid: mp 246–247 °C; IR (KBr): υ_{max} (cm^{-1}) 2231, 1443; ^{1}H NMR (200 MHz, DMSO-d6) δ (ppm) 9.23 (s, 1H), 8.90 (d, 1H, J = 6.2 Hz), 8.59 (d, 1H; J = 8.0 Hz), 8.11 (t, 1H, J = 8.4 Hz), 8.01 (m, 9H), 7.38 (m, 6H), 7.38 (m, 9H, J = 2.5 Hz), 7.06 (m, 6H, J = 3.6 Hz), 4.28 (s, 3H); ^{13}C NMR (300 MHz, acetone-d6) δ (ppm) 148.2, 147.1, 143.5, 142.8, 137.3, 130.9, 129.0, 128.8, 125.7, 100.9, 84.1, 80.4, 73.4, 61.9, 45.3, 41.0; MS (ESI$^+$) *m*/*z* (relative intensity) 426 (M$^+$, 100); Anal. Calcd for $C_{30}H_{24}N_3I$: C, 65.11; H, 4.37; N, 7.59. Found: C, 65.13; H, 4.39; N, 7.57.

*1-Methyl-3-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-ylethynyl) pyridinium iodide (4d).* Following the general procedure A, from **1a** and 3-Ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), afforded 0.1705 g, (57%) of **4d** as a brown solid: mp 134 °C; IR (KBr): υ_{max} (cm^{-1}) 3419, 2230, 1742; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.45 (s, 1H), 9.01 (d, 1H, J = 6.2 Hz), 8.88 (d, 1H, J = 8.1 Hz), 8.25 (d, 1H, J = 8.4 Hz), 8.19 (dd, 1H, J = 6.2 Hz), 8.03 (d, 1H, J = 7.7 Hz), 7.74 (t, 1H, J = 7.3 Hz), 7.55 (t, 1H, J = 6.9 Hz), 4.51 (s, 3H), 1.78 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 209.1, 149.6, 148.4, 146.6, 141.1, 133.7, 131.3, 129.2, 127.7, 126.2, 124.5, 121.4, 115.9, 88.1, 87.7, 87.5, 48.4, 28.2; HRMS Calcd for $C_{20}H_{20}N_3O_2I$: (M$^+$) 334.1555. Found 334.1523.

*1-Methyl-2-(1-trityl-1*H*-pyrazol-4-ylethynyl) pyridinium iodide (5c).* Following the general procedure A, from **2** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), gave 0.08 g, (45%) of **5c** as a brown solid: mp 233 °C. IR (KBr): υ_{max}

(cm^{-1}) 2215, 1615, 1443; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 8.93 (d, 1H, *J* = 5.8 Hz), 8.51 (t, 1H, *J* = 8.1 Hz), 8.21 (d, 1H, *J* = 7.8 Hz), 8.08 (s, 2H), 7.96 (t, 1H, *J* = 6.2 Hz), 7.41 (t, 9H, *J* = 3.6 Hz), 7.18 (m, 6H), 4.45 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 146.3, 144.0, 142.4, 141.4, 137.4, 137.0, 130.2, 129.1, 127.6, 125.5, 116.5, 98.8, 98.4, 81.8, 78.7, 46.6; MS (ESI$^+$) *m/z* (relative intensity) 426 (M$^+$, 100); Anal. Calcd for $C_{30}H_{24}N_3I$: C, 65.11; H, 4.37; N, 7.59. Found: C, 65.14; H, 4.34; N, 7.63.

*1-Methyl-2-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-ylethynyl) pyridinium iodide (**5d**).* Following the general procedure A, from **2** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), gave 0.1705 g, (53%) of **5d** as an orange solid: mp 185 °C; IR (KBr): υ$_{max}$ (cm^{-1}) 3418, 2350, 1628; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 9.18 (d, 1H, *J* = 6.6 Hz), 8.79 (t, 1H, *J* = 6.6 Hz), 8.38 (d, 1H, *J* = 8.1 Hz), 8.19 (t, 1H, *J* = 7.7 Hz), 7.94 (d,1 H, *J* = 8.1 Hz), 7.73 (td, 2H, *J* = 1.1, 7.3 Hz), 7.60 (td, 1H, *J* = 1.8, 4.4 Hz), 4.44 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 209.0, 148.3, 148.3, 146.5, 141.1, 136.0, 130.3, 126.9, 126.7, 125.5, 125.1, 120.8, 111.4, 100.2, 95.6, 46.8, 17.8, 11.2; HRMS Calcd for $C_{20}H_{20}N_3O_2I$: (M$^+$) 334.1555. Found 334.1547.

*1-Methyl-4-(1-trityl-1*H*-pyrazol-4-ylethynyl)pyridinium hexafluoro phosphate (**6c**).* Following the general procedure A, from **3** and 4-ethynyl-1-trityl-1*H*-pyrazol (0.7551 mmol, 0.2626 g), afforded 0.2485 g, (77%) of **6c** as an orange solid: mp 249–251 °C; IR (KBr): υ$_{max}$ (cm^{-1}) 2215, 1637, 1447; ^{1}H NMR (200 MHz, DMSO-d6) δ (ppm) 8.89 (d, 2H, *J* = 6.7 Hz), 8.09(d, 2H, *J* = 7.1 Hz), 7.93 (s, 1H), 7.39 (m, 10H), 7.06 (m, 6H), 4.25 (s, 3H); ^{13}C NMR (300 MHz, acetone-d6) δ (ppm) 146.2, 143.3, 141.2, 138.3, 130.8, 129.3, 128.9, 128.7, 100.7, 97.8, 80.0, 73.3, 48.7; MS (ESI$^+$) *m/z* (relative intensity) 426 (M$^+$, 100); Anal. Calcd for $C_{30}H_{24}N_3PF_6$: C, 63.05; H, 4.23; N, 7.35. Found: C, 63.07; H, 4.27; N, 7.33.

*1-Methyl-4-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (**6d**).* Following the general procedure A, from **3** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (0.7551 mmol, 0.1736 g), gave 0.2066 g, (69%) of **6d** as a black solid: mp 144 °C; IR (KBr): υ$_{max}$ (cm^{-1}) 3418, 2207, 1636; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 9.02 (d, 2H, *J* = 6.6 Hz), 8.37 (d, 2H, *J* = 6.9 Hz), 8.28 (d, 1H, *J* = 8.4 Hz), 8.06 (d, 1H, *J* = 8.1 Hz), 7.75 (t, 1H, *J* = 7.3 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 4.47 (s, 3H), 1.78 (s, 9H);^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 209.1, 145.5, 143.0, 140.6, 139.8, 129.0, 127.6, 125.1, 122.9, 119.6, 117.1, 110.9, 95.5, 88.7, 69.4, 47.0, 29.9; MS (ESI$^+$) *m/z* (relative intensity) 253 (M$^+$, 100).; Anal. Calcd for $C_{20}H_{21}N_3O_2PF_6$: C, 49.90; H, 4.61; N, 8.73. Found: C, 49.95; H, 4.57; N, 8.76.

Method B (4, 5, 6a–b). Analogously to Method A, with addition of l% LiCl (0.0667 mmol, 0.0026 g and stirring the reaction mixture for 20 h at room temperature.

*1-Methyl -3-(1*H*-pyrrol-3-ylethynyl) pyridinium iodide (**4a**).* Following the general procedure B, from **1a** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), afforded 0.1351 g, (63%) of **4a** as a brown solid: mp 133 °C; IR (KBr): υ$_{max}$ (cm^{-1}) 3444, 3131, 2208, 1637; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 8.66 (d, 2H, *J* = 6.7 Hz), 7.90 (d, 2H, *J* = 6.7 Hz), 7.36 (t, 1H, *J* = 1.4 Hz), 6.85 (dd, 1H, *J* = 0.7, 2.0 Hz), 6.44 (dd, 1H, *J* = 1.2, 1.4 Hz), 4.89 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 145.7, 144.6, 132.9, 129.7, 127.5, 124.6, 120.5, 118.3, 112.9, 106.8, 47.8; MS (ESI$^+$) *m/z* (relative intensity) 341 (M$^+$, 100); Anal. Calcd for $C_{12}H_{11}N_2I$: C, 46.32; H, 3.89; N, 9.00. Found: C, 46.29; H, 3.87; N, 9.03.

*1-Methyl-3-[1-(toluene-4-sulfonyl)-1*H*-indol-3-ylethynyl] pyridinium iodide (**4b**).* Following the general procedure B, from **1a** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.2231 g), gave 0.1489 g, (61%) of **4b** brown solid: mp 208 °C; IR (KBr) : υ$_{max}$ (cm^{-1}) 3505, 2231, 1378; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 8.84 (d, 2H, *J* = 6.7 Hz), 8.34 (s, 1H), 8.14 (d, 2H, *J* = 6.9 Hz), 8.03 (t, 2H, *J* = 8.6 Hz), 7.94 (d, 2H; *J* = 8.4 Hz), 7.80 (d, 1H; *J* = 0.9 Hz), 7.70-7.58 (m, 4H), 4.4 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 147.3, 146.3, 134.8, 133.7, 133.0, 132.6, 132.5, 131.2, 129.7, 129.6, 129.5, 128.1, 127.0, 126.6, 125.4, 121.2, 114.6, 90.57, 48.8, 47.6, 21.4; MS (ESI$^+$) *m/z* (relative intensity) 388 (M$^+$, 100); Anal. Calcd for $C_{23}H_{20}N_2O_3SI$: C, 51.99; H, 3.79; N, 5.27. Found: C, 51.97; H, 3.83; N, 5.25.

*1-Methyl-2-(1*H*-pyrrol-3-ylethynyl) pyridinium iodide (**5a**).* Following the general procedure B, from **2** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), gave 0.0381 g, (26%) of **5a** as an orange dark oil: IR (KBr): υ$_{max}$ (cm^{-1}) 3434, 2206, 1619; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 8.88 (d, 1H; *J* = 7.2 Hz), 8.45 (t, 1H, *J* = 6.8 Hz), 8.13 (d, 1H, *J* = 8.0 Hz), 7.87 (t, 1H, *J* = 6.2 Hz), 7.50 (t, 1H, *J* = 1.6 Hz), 6.89 (dd, 1H, *J* = 0.9, 2.0 Hz), 6.53 (dd, 1H, *J* = 1.4, 2.9 Hz), 4.46 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 147.1, 145.2, 141.1, 131.5, 128.2, 125.7, 120.9, 113.0, 109.5, 101.3, 81.6, 47.86; MS (ESI$^+$) *m/z* (relative intensity) 341 (M$^+$, 100); Anal. Calcd for $C_{12}H_{11}N_2I$: C, 46.32; H, 3.89; N, 9.00. Found: C, 46.33; H, 3.85; N, 9.02.

*1-Methyl-2-[1-(toluene-4-sulfonyl)-1*H*-indol-3-ylethynyl] pyridinium iodide (**5b**).* Following the general procedure B, from **2** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.2231 g), afforded 0.2387 g, (70%) of **5b** as a yellow solid: mp 192 °C. IR (KBr): υ$_{max}$ (cm^{-1}) 3500, 2220, 1378; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 9.02 (d, 1H, *J* = 6.7 Hz), 8.58 (t, 1H, *J* = 7.1 Hz), 8.49 (s, 1H), 8.37 (d, 1H, *J* = 7.7 Hz), 8.09 (d, 1H, *J* = 7.8 Hz), 8.03 (t, 1H, *J* = 6.2 Hz), 7.97 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 7.5 Hz), 7.54–7.47 (m, 2H), 7.44 (t, 3H, *J* = 8.4 Hz), 4.59 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 148.0, 147.9, 145.9, 135.6, 135.5, 135.1, 132.7, 131.4, 130.8, 128.4, 127.4, 125.8, 121.3, 115.0, 102.3, 101.1, 85.2, 48.1, 47.9, 21.5; MS (ESI$^+$) *m/z* (relative intensity) 388 (M$^+$, 100); Anal. Calcd for $C_{23}H_{20}N_2O_3SI$: C, 51.99; H, 3.79; N, 5.27. Found: C, 51.97; H, 3.83; N, 5.25.

*1-Methyl-4-(1*H*-pyrrol-3-ylethynyl) pyridinium hexafluoro phosphate (**6a**).* Following the general procedure B, from **3** and 3-ethynyl-1-triisopropylsilanyl-1*H*-pyrrole (0.7551 mmol, 0.1875 g), gave 0.0379 g, (32%) of **6a** as a brown solid: mp 133 °C; IR (KBr): υ$_{max}$ (cm^{-1}) 3444, 3131, 2208, 1637; ^{1}H NMR (200 MHz, CD$_3$OD) δ (ppm) 8.66 (d, 2H, *J* = 6.7 Hz), 7.89 (d, 2H, *J* = 6.7 Hz), 7.36 (t, 1H, *J* = 1.4 Hz), 6.85 (dd, 1H, *J* = 0.7, 2.0 Hz), 6.44 (dd, 1H, *J* = 1.3, 1.4 Hz), 4.89 (s, 3H); ^{13}C NMR (300 MHz, CD$_3$OD) δ (ppm) 145.7, 144.6, 132.9, 129.7, 127.5, 124.6, 120.5, 118.3, 112.9, 106.8, 47.8; MS (ESI$^+$) *m/z* (relative intensity) 341 (M$^+$, 100); Anal. Calcd for

$C_{12}H_{11}N_2PF_6$: C, 43.92; H, 3.38; N, 8.54. Found: C, 43.97; H, 3.34; N, 8.55.

*1-Methyl-4-[1-(toluene-4-sulfonyl)-1*H*-indol-3-ylethynyl] pyridinium hexafluorophosphate (**6b**).* Following the general procedure B, from **3** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (0.7551 mmol, 0.0.2231 g), gave 0.1692 g, (50%) of **6b** as a brown solid: mp 208 °C; IR (KBr): υ_{max} (cm^{-1}) 3564, 2238, 1384. ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 8.84 (d, 2H, J = 6.7 Hz), 8.34 (s, 1H), 8.14 (d, 2H, J = 6.9 Hz), 8.03 (t, 2H, J = 8.6 Hz), 7.94 (d, 2H; J = 8.4 Hz), 7.80 (d, 1H; J = 0.9 Hz), 7.70–7.58 (m, 4H), 4.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 147.3, 146.3, 134.8, 133.7, 133.0, 132.6, 132.5, 131.2, 129.7, 129.6, 129.5, 128.1, 127.0, 126.6, 125.4, 121.2, 114.6, 90.5, 48.8, 47.6, 21.4; MS (ESI$^+$) m/z (relative intensity) 388 (M$^+$, 100); Anal. Calcd for $C_{23}H_{20}N_2O_2SPF_6$: C, 50.37; H, 3.49; N, 5.11. Found: C, 50.42; H, 3.51; N, 5.07.

General procedure for the synthesis of D-π-A+-π-D pyridinium salts (7a–d)

Method C. A flame-dried flask was charged under argon with 1 equiv. of the corresponding 3,5-dibromo-*N*-butylpyridinium hexafluoro-phosphate salt (0.3 g, 0.6834 mmol), 10 mol% CuI (0.013 g, 0.0683 mmol), 5 mol% $PdCl(PPh_3)_2$ (0.0239 g, 0.0341 mmol) in dry THF (10 mL) were added. The corresponding acetylene heterocycle (2.4 equiv., 1.6401 mmol) and Et_3N (3 equiv., 2.0502 mmol, 0.2815 mL) were added and the mixture was stirred at room temperature for 1 h. Work-up following Method A or B.

*1-Butyl-3,5-(1*H*-pyrrol-3-ethynyl) pyridinium hexafluorophosphate (**7a**).* Following the general procedure C, **1b** and 3-ethynyl-1-triisopropyl silanyl-1*H*-pyrrole (1.6401 mmol, 0.4074 g), gave 0.1714 g, (55%) of **7a** as a brown solid: mp decomposed at 210 °C; IR (KBr): υ_{max} (cm^{-1}) 3444, 2965, 2215; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.15 (d, 2H, J = 1.4 Hz), 8.54 (s, 1H), 7.32 (dd, 2H, J = 1.2, 1.4 Hz), 6.91 (dd, 2H, J = 2.0, 2.5 Hz), 6.35 (t, 2H, J = 2.5 Hz), 4.84 (t, 2H; J = 7.5 Hz), 2.22–2.20 (m, 2H, J = 8.0 Hz), 1.53–1.50 (m, 2H), 0.99 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 145.7, 143.1, 126.1, 124.8, 119.4, 111.3, 101.5, 96.2, 80.8, 62.4, 32.9, 19.1, 12.8; MS (ESI$^+$) m/z (relative intensity) 314 (M$^+$, 100); Anal. Calcd for $C_{21}H_{20}N_3PF_6$: C 54.91; H, 4.39; N, 9.15. Found: C, 54.92; H, 4.36; N, 9.14.

*1-Butyl-3,5-[1-(toluene-4-sulfonyl)-3-ethynylindole] pyridinium hexafluorophosphate (**7b**).* Following the general procedure C, from **1b** and 3-ethynyl-1-(toluene-4-sulfonyl)-1*H*-indole (1.6401 mmol, 0.4846 g), afforded 0.4778 g, (83%) of **7b** as a brown solid: mp 177 °C. IR (KBr) υ_{max} (cm^{-1}) 2220; 1373; ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 9.45 (d, 2H, J = 1.5 Hz), 9.02 (s, 1H), 8.21 (s, 2H), 8.09 (d, 2H, J = 8.2 Hz), 7.99 (d, 4H; J = 8.5 Hz), 7.79 (d, 2H; J = 6.9 Hz), 7.54–7.37 (m, 9H), 4.92 (t, 2H, J = 7.6 Hz), 2.37 (s, 6H), 2.20–2.06 (m, 2H), 1.53–1.48 (m, 2H), 1.01 (t, 3H, J = 7.6 Hz); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 148.4, 147.3, 146.0, 135.2, 134.9, 132.4, 131.3, 130.8, 128.1, 127.1, 125.7, 125.3, 121.3, 114.7, 103.5, 90.6, 86.9, 63.7, 33.8, 21.5, 20.0, 13.7; MS (ESI$^+$) m/z (relative intensity) 722 (M$^+$, 100); Anal. Calcd for $C_{43}H_{37}N_3O_6S_2PF_6$: C, 57.39; H, 4.03; N 4.67. Found: C, 57.37; H, 4.04; N, 4.68.

*1-Butyl-3,5-(1-trityl-1*H*-pyrazol-4-ylethynyl)pyridinium hexafluorophosphate (**7c**).* Following the general procedure C, from **1b** and 4-ethynyl-1-trityl-1*H*-pyrazol (1.6401 mmol, 0.5711 g), gave 0.5317 g, (80%) of **7c** as a brown solid: mp decomposes at 230 °C; IR (KBr): υ_{max} (cm^{-1}) 2223, 1618; ^{1}H NMR (200 MHz, DMSO-d$_6$) δ (ppm) 9.20 (s, 2H), 8.59 (s, 1H), 7.80 (s, 2H), 7.70 (s, 2H), 7.41–7.38 (m, 15H), 7.17– 7.14 (m, 10H), 7.30–7.28 (m, 5H), 4.79 (t, 2H, J = 3.6 Hz), 4.28 (s, 3H); ^{13}C NMR (300 MHz, acetone-d$_6$) δ (ppm) 147.9, 146.8, 144.4, 142.6, 141.9, 136.5, 131.8, 130.0, 128.1, 127.9, 127.8, 127.5, 126.7, 125.1, 99.9, 90.4, 83.1, 79.5, 62.6, 19.1, 12.7; MS (ESI$^+$) m/z (relative intensity) 801 (M$^+$, 100); Anal. Calcd for $C_{57}H_{46}N_5PF_6$: C, 72.37; H, 4.90; N, 7.40. Found: C, 72.34; H, 4.94; N, 7.42.

*1-Butyl-3,5-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-ylethynyl) pyridinium hexafluoro phosphate (**7d**).* Following the general procedure C, from **1b** and 3-ethynyl-indazole-1-carboxylic acid *tert*-butyl ester (1.6401 mmol, 0.3772 g), gave 0.2315 g, (55%) of **7d** as a black solid: mp: decomposes at 240 °C; IR (KBr): υ_{max} (cm^{-1}) 2229; 1744; 1382; ^{1}H NMR (200 MHz, acetone-d$_6$) δ (ppm) 9.69 (d, 2H, J = 1.2 Hz), 9.37 (s, 1H), 8.27 (d, 2H, J = 8.5 Hz), 8.03 (d, 2H, J = 7.9 Hz), 7.73 (t, 2H, J = 6.9 Hz), 7.52 (t, 2H, J = 7.3 Hz), 4.90 (t, 2H, J = 7.6 Hz), 2.23–2.20 (m, 2H), 1.53–1.48 (m, 2H, J = 7.3 Hz), 1.02 (t, 3H, J = 7.6 Hz); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 150.0, 149.1, 147.8, 140.8, 132.8, 130.8, 127.5, 125.8, 124.7, 121.1, 115.8, 88.6, 87.4, 86.5, 64.0, 33.7, 28.2, 20.1, 13.7; MS (ESI$^+$) m/z (relative intensity) 616 (M$^+$, 100); Anal. Calcd for $C_{37}H_{43}N_5O_4PF_6$: C, 58.04; H, 5.53; N, 9.15. Found: C, 58.02; H, 5.57; N, 9.12.

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