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## PAPER

Synthesis of charged bis-heteroaryl donor–acceptor (D–A<sup>+</sup>) NLO-phores coupling ( $\pi$ -deficient– $\pi$ -excessive) heteroaromatic rings†

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Charged chromophores based on heteroaromatic cations were prepared by reaction of alkylazinium salts with *N*-heteroarylstannanes under Stille conditions. This approach provides easy access to potential single donor D–A<sup>+</sup> chromophores in which the acceptor moiety A<sup>+</sup> is the pyridinium cation and the donors are different  $\pi$ -excessive *N*-heterocycles. The  $\beta$  hyperpolarizabilities were measured in 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 and correlated Hartree–Fock-based methods. In some chromophores, the absence of a bridge between donor and acceptor fragments increases the NLO properties.

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## Introduction

There is considerable interest in the design and synthesis of conjugated donor–acceptor (D–A) organic molecules with non-linear optical (NLO)<sup>1</sup> properties owing to their applications in areas such as optoelectronics,<sup>2</sup> all-optical data processing technology, biological imaging<sup>3</sup> and dye-sensitized solar cells,<sup>4</sup> *inter alia*. In an effort to achieve large optical nonlinearities, with large second-order polarizabilities, related to an electronic intramolecular charge transfer (ICT) effect, a number of organic compounds have been studied as possible NLO materials.

Numerous examples of different D–A chromophores contain olefinic or aromatic linkers in the conjugated bridge along with *N,N*-disubstituted anilines as electron donors, but only recently have cationic acceptors been employed. A significant feature of these charged molecules is that the nature of the counterion of the organic salt influences the crystal structure and can be used to modify crystal packing. By tuning

their solubility, potential applications in imaging can also be achieved. Other potential advantages of cationic chromophores include their greater stability and higher chromophore number densities when compared with other NLO materials. Amongst the cationic chromophores reported to date, charged acceptor units are well represented by benzothiazolium<sup>5</sup> and pyridinium salts.<sup>6</sup> The latter compounds have received significant attention as 1D (D– $\pi$ -A<sup>+</sup>) molecules and 2D (D– $\pi$ -A<sup>+</sup>– $\pi$ -D) pyridinium-based chromophores, which are represented, respectively, by the commercialized DAST and DSTMS,<sup>7</sup> and diquats<sup>8</sup> that are of interest in emerging fields<sup>9</sup> and are used for terahertz (THz) wave generation of different frequencies by mixing of two lasers.<sup>10</sup> Recently, we reported the use of the quinolizinium system<sup>11</sup> (Fig. 1) as a marker in nonlinear optical bioimaging by a multiphotonic interaction such as TPA (two-photon absorption)<sup>12</sup> and we also described detailed structure–property relationship studies on the donor (D)–azinium acceptor (A<sup>+</sup>), specifically in the (D– $\pi$ -A<sup>+</sup>) and (D– $\pi$ -A<sup>+</sup>– $\pi$ -D) chromophores represented in Fig. 2.<sup>13</sup>

Our interest in the chemistry of heteroaromatic cations led us to explore palladium-catalyzed cross-coupling reactions as efficient strategies to generate a variety of new cationic chromophores in which the cationic acceptor unit is linked to the donor unit through single, double and triple bonds<sup>14</sup> thus allowing us to undertake comparative studies on the NLO properties of azinium, azolium and quinolizinium-based push–pull chromophores.

As a continuation of our research on the applications of heteroaromatic cations in the NLO field we decided to explore

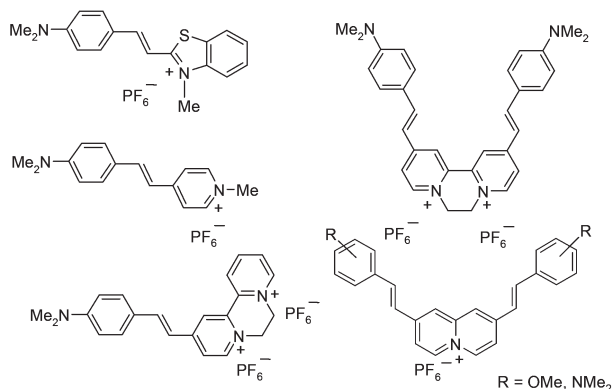
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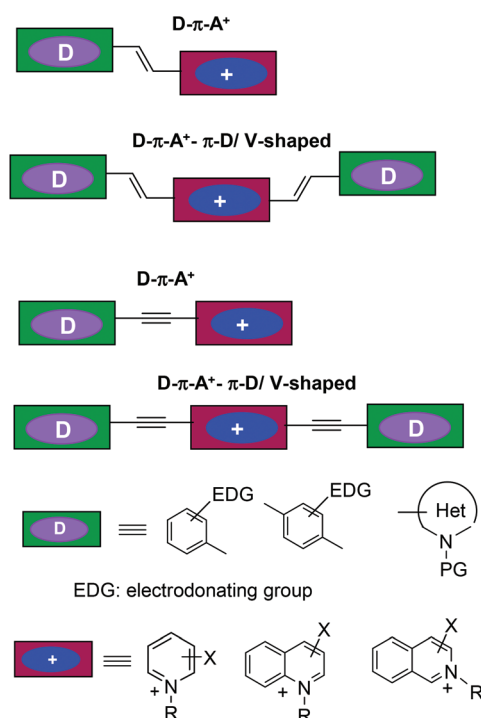
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†Electronic supplementary information (ESI) available: Copies of <sup>1</sup>H and <sup>13</sup>C NMR for all new compounds reported and general information of OL and NLO properties. See DOI: 10.1039/c3ob41159a



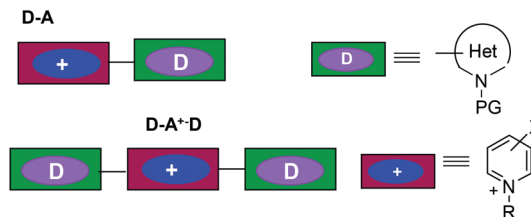
**Fig. 1** Examples of 1D (D- $\pi$ -A $^+$ ) and 2D (D- $\pi$ -A $^+$ - $\pi$ -D) chromophores based on heteroaromatic cations as acceptor units.



**Fig. 2** (D- $\pi$ -A $^+$ ) and (D- $\pi$ -A $^+$ - $\pi$ -D) chromophores based on azinium cations as acceptor units.

new chromophores generated by direct coupling of a  $\pi$ -deficient heteroaromatic cation to a  $\pi$ -excessive heterocycle, a kind of molecule that rarely appears in NLO references.<sup>15</sup> We prepared different pyridinium-based chromophores that were inherently polarized by connecting heteroaromatic rings with different D-A $^+$  electron densities. The linear optical (LO) and NLO properties were compared with those of chromophores such as the ones shown in Fig. 2, in which the A $^+$  moiety is connected to the  $\pi$ -electron donor *via* a  $\pi$ -conjugated bridge.

We report here the synthesis of a series of charged chromophores (D-A $^+$ , Fig. 3) by Stille<sup>16</sup> cross-coupling reactions to give *push-pull* molecules that combine the charged heteroaromatic



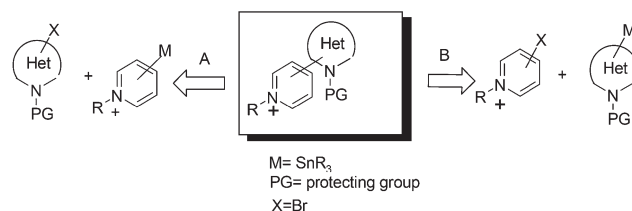
**Fig. 3** Push-pull D-A $^+$  chromophores by coupling a  $\pi$ -deficient charged heteroaromatic cation to a  $\pi$ -excessive heteroarene.

cations employed as acceptor units (A $^+$ ) with  $\pi$ -excessive *N*-heterocycles as donor units (D). These units are connected by a  $\sigma$  bond, giving rise to chromophores with  $\beta$  values higher than expected. The resulting D-A $^+$  chromophores were studied by hyper-Rayleigh scattering experiments and by theoretical analysis, including density functional theory (DFT) and correlated Hartree-Fock-based methods (RCIS(D)).

## Results and discussion

The synthesis of chromophores with the general structure D-A $^+$  (Fig. 3) was carried out on the 2-, 3- or 4-bromo-*N*-methyl pyridinium salts. The strategy to obtain the D-A $^+$  chromophores involved either conversion of the *N*-methyl pyridinium derivatives into the corresponding metallated cation, in order to assess the Stille reaction with a variety of heteroaryl halides (route A in Scheme 1), or reaction of the corresponding bromopyridinium derivatives with different *N*-heteroaryl stannanes (route B in Scheme 1). The former approach, reported by Zoltewicz *et al.*,<sup>17</sup> involved quaternization of the corresponding pyridyl stannane with methyl iodide. However, the preparation of metallated pyridinium by reaction of either the lithiated heterocycle with trialkyltin chloride or by a palladium-coupling reaction between a haloheteroaromatic cation and hexaalkyl-distannane suffers from several disadvantages, including low solubility of the salts in solvents suitable for organolithium reagents, sensitivity of the substrate to nucleophilic attack, or poor selectivity of the lithiation reaction. For this reason, we used the heteroaromatic cation as the electrophilic partner (route B).

Initially, starting from 3-bromopyridinium bromide (1), the conditions described for palladium-promoted coupling



**Scheme 1** Alternative strategies for the synthesis of 4-6 by Stille reaction.

reactions on quinolinizinium salts<sup>18</sup> were adapted and optimized for **1** by using tributylstannanyl-(1-*tert*-butyldimethylsilyl)-1*H*-indole, Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%) and copper iodide as co-catalysts (10 mol%) in DMF (Method A). After stirring the reaction mixture for 20 h at room temperature, traces of coupling product **4b** were observed by NMR, together with the dehalogenated product from salt **1**, which is the major product even on heating at 65 °C. The best conditions to obtain **4b** (51% yield, Table 1) involved the use of Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub> (5 mol%), CuI (10 mol%) in DMF with stirring for 20 h at room temperature or heating at 65 °C for 4 h (Method B). Coupling of **1** with tributylstannanyl-1-trityl-1*H*-pyrazole afforded **4c** in 53% yield using either [Pd(PPh<sub>3</sub>)<sub>4</sub> or Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub>]. We proceeded to use Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI/DMF/65 °C (Method A) or Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub>/DMF/65 °C (Method B) to produce a variety of coupled products (see Table 1). However, when Method A was applied to pyrrole and indole derivatives, the dehalogenated pyridinium salt was obtained both at room temperature and on

heating at 65 °C for 20 h. Consequently, Method B was applied and this generated **4a–b** with loss of the protecting group and in consistent yields on stirring at room temperature or on heating at 65 °C.

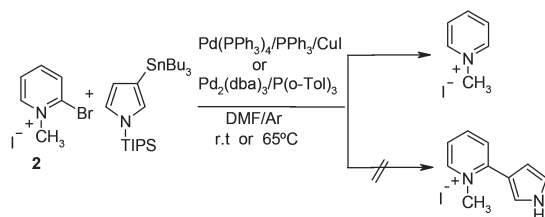
The coupling of **1** with 3-tributylstannylindazol-1-carbamic acid *tert*-butyl ester gave a better yield when using Method A (*i.e.* room temperature). On heating the reaction mixture at 65 °C, decomposition products were obtained along with the corresponding dehalogenated pyridinium salt. Furthermore, deprotection of the (Boc-) group in **4d** was observed during the purification process. On examining the two methods (A or B) for the coupling on C-2, it was found that coupling of **2** with the corresponding pyrrole and indole stannanes gave the dehalogenated pyridinium salt as the main product. All attempts to minimize the dehalogenation process and the concomitant formation of the 1-methylpyridinium salt proved unsuccessful (Scheme 2). The other coupling reactions gave lower yields than those for C-3 coupling. Analogous to **4d**, product **5d** was

**Table 1** Stille reaction on bromo-1-methylpyridinium salts (**1–3**) with heteroaryl stannanes

<p> <b>1:</b> X = 3-Br  <b>2:</b> X = 2-Br  <b>3:</b> X = 4-Br         </p> <p><b>4,5,6a-d</b></p>				
Entry	Stannane	Products <b>4–6(a–d)</b> Yield (%)		
1		 <b>4a</b> (13%) <sup>b</sup>	 <b>5a</b> (–) <sup>a,b</sup>	 <b>6a</b> (98%) <sup>b</sup>
2		 <b>4b</b> (51%) <sup>b</sup>	 <b>5b</b> (–) <sup>a,b</sup>	 <b>6b</b> (78%) <sup>b</sup>
3		 <b>4c</b> (53%) <sup>a</sup>	 <b>5c</b> (34%) <sup>a</sup>	 <b>6c</b> (91%) <sup>a</sup>
4		 <b>4d</b> (33%) <sup>c</sup>	 <b>5d</b> (31%) <sup>c</sup>	 <b>6d</b> (90%) <sup>c</sup>

For all compounds, yields are given for isolated products. TIPS: triisopropylsilyl; TBS: *tert*-butyldimethylsilyl; Tr: trityl; Boc: *tert*-butoxycarbonyl.

<sup>a</sup>Method A: Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI/DMF/65 °C. <sup>b</sup>Method B: Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub>/DMF/65 °C.



Scheme 2 Stille reaction of **2** and *N*-protected 3-tributylstannylpyrrole.

obtained in higher yield at room temperature. The yields of products from **3** as the iodide were poor due to low solubility and difficult purification. The PF<sub>6</sub> salt of **3** was prepared in an effort to overcome these problems. In this case, the yields of the coupling with **3** as the hexafluorophosphate salt were in the range 78–98%. Analogously, the coupling with pyrrole and indole (**6a–b**) led to the product with loss of the protecting groups. Furthermore, compound **6d** was obtained in better yield on applying Method A at room temperature. The results are summarized in Table 1. From a synthetic point of view, the Stille reaction of D–A<sup>+</sup> systems was efficient when using Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI/DMF (Method A) for the C3 position (less activated). For the 2-bromopyridinium salts, however, the results can be related to the activation of the α-position and the instability of the resulting products. In the case of 4-bromopyridinium salts, Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-Tol)<sub>3</sub>/DMF (Method B) gave better yields at 65 °C for pyrrole and indole and at room temperature for indazole.

### Linear optical properties

The absorption spectra of compounds **4–6** were monitored in the 230–800 nm range. It can be seen in Fig. 4 that the compounds did not exhibit significant absorption above 450 nm. The relatively intense peak at the longest wavelengths, which appeared in the 250–425 nm range depending on the system, was ascribed to the π–π\* intramolecular charge transfer (ITC) absorption band. The location of the maximum of this band is usually rather sensitive to the degree of conjugation and electron-donating character of the *N*-heterocycle substituted at the pyridinium acceptor moiety. Most of the chromophores – with the exception of **4a–c** (288, 288 and 320 nm) and **5d** (375 nm), which showed a relatively weak broadening of the absorption

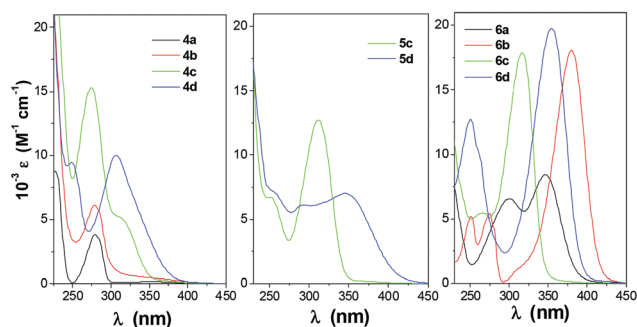


Fig. 4 Absorption spectra of compounds **4–6** in methanol at 25 °C.

to the red (centered at the indicated wavelength) – exhibited a sharp cut-off for the π–π\* transition band (Fig. 4). The mentioned broadening, which was also observed earlier for similar compounds, where the acceptor pyridinium moiety (A<sup>+</sup>) was connected to the donor (D) via a π-conjugated bridge instead of directly,<sup>13a</sup> can be attributed to the overlapping of the usually weak n–π\* transition due to the presence of N heteroatoms.

A good correlation was found between the degree of conjugation and the stability of the π–π\* ITC transition band. In fact, a considerable bathochromic effect was exerted on this band when (pyrrole, indole, pyrazole and indazole) donor moieties were substituted at the C4(γ) position of the pyridinium unit, while the donors on C3(β) were significantly less efficient. The effect at the C2(α) position is usually somewhere in between the two outlined above due to electronic and steric effects. Therefore, the location of the absorption maximum for each particular donor substituent was in the order λ<sub>max,6</sub> > λ<sub>max,5</sub> > λ<sub>max,4</sub> (see Fig. 4 and Table 2). It is also remarkable that the molar absorptivity values for the maxima of the π–π\* transition are also larger for compounds (**6**) where the donors are substituted at C4(γ) of the pyridinium acceptor. 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 π–π\* ITC absorption band also correlated quite well. The conjugation of compounds **4**, with donors on the C3 of the pyridinium, was less efficient. The pyrazole substituent (**4c**), which is the weakest donor, gave the shortest λ<sub>max</sub> (274 nm) for the π–π\* transition, while indazole (**4d**), one of the best donors, gave the highest λ<sub>max</sub> (307 nm). The absorption maxima for pyrrole and indole substituents (the latter is also a relatively good donor) appeared somewhere in between and had the same λ<sub>max</sub> (279 nm).

Another series of compounds substituted at the *para* C4(γ) position (**6a–d**), the conjugation of which is the most efficient,

Table 2 Linear optical data for **4–6**<sup>a</sup>

Comp.	λ <sub>max</sub>	λ <sub>exc</sub>	λ <sub>em</sub>	ε (M <sup>-1</sup> cm <sup>-1</sup> )	Φ <sub>f</sub> × (10 <sup>-2</sup> )	⟨τ⟩ (ns)
<b>4a</b>	279	—	—	3800	—	—
<b>4b</b>	279	350	540	6150	0.7	3.1
<b>4c</b>	274	310	423	15 300	32.3	14.7
<b>4d</b>	307	350	491	10 000	0.1	2.0
<b>5c</b>	312	310	396	12 353	15.8	0.3
<b>5d</b>	345	—	—	7000	—	—
<b>6a</b>	346	350	491	8450	0.03	0.3
<b>6b</b>	380	350	453	18 050	62.8	6.5
<b>6c</b>	316	310	382	17 900	3.2	0.8
<b>6d</b>	355	350	—	19 750	—	—

<sup>a</sup>The wavelengths of the maxima of the π–π\* charge transfer absorption (λ<sub>max</sub>) and emission (λ<sub>em</sub>) bands upon excitation of λ<sub>exc</sub>, molar absorptivity (ε), fluorescence quantum yields (Φ<sub>f</sub>) were obtained upon excitation at the selected wavelength (λ<sub>exc</sub>) at 25 °C by using a quinine sulphate solution in 0.1 M H<sub>2</sub>SO<sub>4</sub> as a standard and weighted average lifetimes ⟨τ⟩ (defined in the ESI) for compounds in methanol at 25 °C. Excitation for the time-resolved measurements was carried out using a sub-nanosecond pulsed NanoLED emitting at 335 nm.



did not diverge significantly from this trend. As expected, the weakest donor (pyrazole, **6c**) gave the shortest  $\lambda_{\max}$  (316 nm) and the longest wavelengths for the absorption maxima ( $\lambda_{\max}$ ) were obtained for indole **6b** (380 nm) and indazole **6d** (355 nm), which are the most efficient donors. Pyridinium compounds substituted at C2( $\alpha$ ) (**5c** and **5d**) followed the expected behaviour. Comparison of the (D-A<sup>+</sup>) and (D- $\pi$ -A<sup>+</sup>) results led to rather similar conclusions, namely, (i) donor substituents at the C4 ( $\gamma$ ) resulted in the most efficient conjugation, while the one at C3( $\beta$ ) is less efficient, (ii) pyrazole is the weakest donor, whereas indole and indazole are the most efficient ones, and (iii) in general the effect on conjugation and stabilization of the donor position at the pyridinium moiety seems to be greater than that due to its relative donor strength capability. However, quantitatively the absence of the  $\pi$ -conjugated bridge between D and A<sup>+</sup> units leads to a loss of conjugation which translates into a hypsochromic displacement of the  $\lambda_{\max}$  for the  $\pi \rightarrow \pi^*$  transition, which in some cases reaches  $\sim 60$  nm, and a decrease in the molar absorptivity values for this maximum. Note that **6b** and **6d** are the exceptions, where the absence of the  $\pi$ -conjugated bridge makes molar absorptivities increase.

Fluorescence quantum yields ( $\Phi_f$ ) obtained from the analysis of the emission spectra depicted in Fig. 5 by using a quinine sulphate solution in 0.1 M H<sub>2</sub>SO<sub>4</sub> as a standard<sup>19</sup> are presented in Table 2. With the exception of **4c**, **5c** and **6b**, all compounds exhibited null or very low fluorescence quantum yields. Among the fluorescent systems, clear correlations between  $\lambda_{\text{em}}$  and the electron-donating characteristics of the substituent and/or its position on the pyridinium ring were not observed. All the fluorescence intensity profiles for the fluorescent samples, measured at  $\lambda_{\text{em}}$  upon excitation at 335 nm, were complex – apart from that of **4c**, which showed monoexponential decay. The profiles can be fitted to bi- or three-exponential decays. This indicates the involvement of some processes other than the simple radiative emission from the singlet to the ground state. As stated before, for other similar systems<sup>13a</sup> it is also quite difficult to assign any correlation between the quantitative values for  $\Phi_f$  and lifetime

averages ( $\langle\tau\rangle$ ) (Table 2), the electron-donating character, the location of the donor substituent or the presence or not of donor-to-acceptor- $\pi$  conjugated bridges, for systems where complex deactivation processes take place.

## Non-linear optical properties

### Hyper-Rayleigh scattering (HRS) measurements

Femtosecond hyper-Rayleigh scattering measurements performed at 800 nm for all compounds (see 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 trends already observed in the linear optical absorption experiments, the largest first hyperpolarizability values were found for indole (**6b**:  $\beta = 142 \times 10^{-30}$  esu) and indazole (**6d**:  $74 \times 10^{-30}$  esu) derivatives. In agreement with the greater influence of the position of the donor substituent at the pyridinium acceptor, which is more marked than the largest relative electron-donating strength characteristics, and the better conjugation and stabilization, the largest molar absorptivities and the largest  $\beta$  values correspond to the compounds with substituents at the C4( $\gamma$ ) positions on the pyridinium system, thus confirming that the best conjugation and charge transfer from the donor to the acceptor is achieved in these positions. For chromophores **6b** and **6d** the obtained hyperpolarizability values are larger than those for the corresponding triple-bond-bridged systems,<sup>13a</sup> a result that could be explained by a more efficient charge transfer between HOMO–LUMO in these non-bridged systems.

### Theoretical studies

Different theoretical approaches were used depending on the spectroscopic property under investigation. The relatively large size of the studied systems places most of the *ab initio* techniques outside the scope of applicability. Configuration interaction with single and double excitation methods (CIS(D)) and time-dependent density functional theory (TDDFT) seem

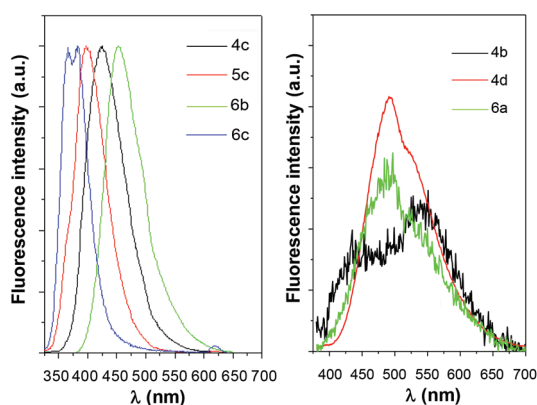


Fig. 5 Fluorescence emission spectra of compounds **4–6** in methanol upon excitation at the selected wavelength  $\lambda_{\text{exc}}$  (Table 2) at 25 °C.

Table 3 Experimental non-linear optical properties of (D-A<sup>+</sup>) **4–6**<sup>a</sup>

Comp.	$\beta_{\text{HRS}}$	$\beta_{\text{zzz}}$	$\beta_{\text{zzz},0}$	$\tau$
<b>4a</b>	14 ± 9	34 ± 23	14 ± 10	—
<b>4b</b>	24 ± 4	58 ± 10	18 ± 3	5 ± 2
<b>4c</b>	14 ± 9	34 ± 24	11 ± 8	3 ± 6
<b>4d</b>	25 ± 2	60 ± 4	21 ± 2	2 ± 1
<b>5c</b>	17 ± 2	42 ± 4	18 ± 2	0.9 ± 0.2
<b>5d</b>	—	—	—	—
<b>6a</b>	16 ± 9	39 ± 22	7 ± 4	—
<b>6b</b>	142 ± 18	343 ± 44	25 ± 3	—
<b>6c</b>	14 ± 4	34 ± 9	11 ± 3	0.9 ± 0.2
<b>6d</b>	74 ± 6	179 ± 15	33 ± 3	2.4 ± 0.2

<sup>a</sup> Resonance enhanced HRS experimental first hyperpolarizability  $\beta_{\text{HRS}}$  ( $10^{-30}$  esu), resonance enhanced diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz}}$  ( $10^{-30}$  esu), and off-resonance diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz},0}$  ( $10^{-30}$  esu). The values of the fluorescence lifetime,  $\tau$  (ns), are also included for molecules that showed demodulation.

to be the most popular approaches for the calculation of excitation spectra. All theoretical calculations were performed using the Gaussian suite of quantum chemical programs.<sup>20</sup> For all the studied cationic systems, the molecular structures used to compute the Non-Linear Optical (NLO) properties correspond to a minimum energy calculated at the HF/6-31G(d) level. These structures were confirmed as minima by evaluation of the harmonic vibrational frequencies, which all proved to have real values.

For the first excited state of the studied cationic systems, the calculated wavelengths were compared to the experimentally determined values ( $\lambda_{\text{max}}$ , in nm). These wavelengths were estimated by two different approaches: (i) the CIS(D) method, which generally predicts accurately excited states that are mainly one-electron transitions from a single reference ground state (Table 4), and (ii) the time-dependent DFT (TDDFT) scheme using a 6-31G(d) basis set on molecular ground state geometries obtained using Becke's three parameter hybrid exchange correlation (XC) functional, which accounts for long-range interactions, the CAM-B3LYP functional density as implemented in Gaussian (Table 5).

Details of the mathematical procedure to obtain the hyper-Rayleigh hyperpolarizability from molecular first hyperpolarizabilities are reported elsewhere.<sup>13a</sup>

Only the optical properties of cationic chromophores **6a–6d** were calculated because these systems show the most efficient conjugation of the chemical systems studied in this work. The

**Table 4** Theoretical values calculated by the CIS(D) method and MP2 for chromophores **6**<sup>a</sup>

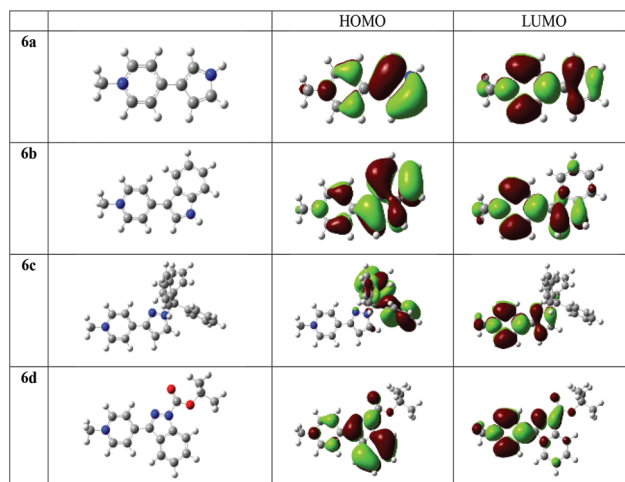
Comp.	$\lambda_{\text{max}}$	$\beta_{\text{HRS}}$	$\beta_{\text{zzz}}$	$\beta_{\text{zzz}, 0}$
<b>6a</b>	311	21	−49	−25
<b>6b</b>	365	44	102	42
<b>6c</b>	316	36	87	44
<b>6d</b>	330	31	68	32

<sup>a</sup> Quantum chemical wavelength of maximum absorption  $\lambda_{\text{max}}$  (nm) calculated by CIS(D), resonance enhanced HRS first hyperpolarizability  $\beta_{\text{HRS}}$  ( $10^{-30}$  esu), resonance enhanced diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz}}$  ( $10^{-30}$  esu), and off-resonance diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz},0}$  ( $10^{-30}$  esu) calculated by MP2 are presented in this table.

**Table 5** Theoretical values predicted by CAM-B3LYP<sup>a</sup>

Comp.	$\lambda_{\text{max}}$	$\beta_{\text{HRS}}$	$\beta_{\text{zzz}}$	$\beta_{\text{zzz}, 0}$
<b>6a</b>	307	20	−49	−18
<b>6b</b>	346	74	175	32
<b>6c</b>	321	48	115	37
<b>6d</b>	335	67	134	30

<sup>a</sup> Theoretical wavelength of maximum absorption  $\lambda_{\text{max}}$  (nm) predicted by TDDFT(CAM-B3LYP), resonance enhanced HRS first hyperpolarizability  $\beta_{\text{HRS}}$  ( $10^{-30}$  esu), resonance enhanced diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz}}$  ( $10^{-30}$  esu), and off-resonance diagonal component of the molecular first hyperpolarizability  $\beta_{\text{zzz},0}$  ( $10^{-30}$  esu) predicted by CAM-B3LYP are presented in this table.



**Fig. 6** HOMO and LUMO of **6a–d** obtained at the CAM-B3LYP/6-31G(d) level of theory.

HOMO and LUMO of cations **6a–6d** are shown in Fig. 6. Excitation between these two MOs generates the  $\pi\text{--}\pi^*$  transition bands and these clearly show the charge transfer from the donor to the acceptor fragments of these systems.

The calculated optical properties of these charged chromophores are collected in Tables 4 and 5. Both CIS(D) and TD-DFT correctly reproduced the  $\lambda_{\text{max}}$  values when compared with the experimental values given in Tables 2 and 3. The theoretically calculated values are lower than the experimental ones by less than 5–10%. This level of agreement was also found elsewhere for different cationic chromophores.<sup>13a</sup> Both theoretical approaches, in agreement with the experimental results, predict the highest hyper-Rayleigh first hyperpolarizability ( $\beta_{\text{HRS}}$ ) for the **6b** system due to the better conjugation and more efficient charge transfer achieved in this chromophore, as discussed previously. A similar result was also obtained for the resonant and off-resonant molecular hyperpolarizabilities  $\beta_{\text{zzz}}$  and  $\beta_{\text{zzz},0}$  respectively. Both theoretical approaches, MP2 and CAM-B3LYP, used to compute the hyperpolarizabilities in Tables 4 and 5 give coherent data and qualitatively reproduce the experimental data presented in Table 3.

The experimental results reported here for cationic chromophores **6** ( $\text{D--A}^+$ ), in relation to ( $\text{D--}\pi\text{--A}^+$ ) reported previously,<sup>13a</sup> reveal that the hyperpolarizability of these dipolar molecules seems to be determined by the strength of its charge-transfer. The largest first hyperpolarizability values were found for indole (**6b**:  $\beta = 142 \times 10^{-30}$  esu) and indazole (**6d**:  $74 \times 10^{-30}$  esu) ( $\text{D--A}^+$ ) chromophores and analogously for the corresponding ( $\text{D--}\pi\text{--A}^+$ ) derivatives indole ( $113 \times 10^{-30}$  esu) and indazole ( $125 \times 10^{-30}$  esu)). In agreement with the greater influence of the position of esu, the donor substituent at the pyridinium acceptor and the better conjugation and stabilization, the largest molar absorptivities and the most favourable  $\beta$  values correspond to the compounds whose substituents are at the C4( $\gamma$ ) position on the pyridinium unit, thus confirming that the best conjugation and charge transfer from the donor

to the acceptor is achieved in this position. However, in the case of indole, the common assumption that  $\beta$  can be maximized using a conjugated bridge<sup>21</sup> to link D and A acceptor units is not clear because, surprisingly, the highest hyperpolarizability<sup>22</sup> was found for indole donor **6b**, which has a linear (D-A<sup>+</sup>) geometry connected by a  $\sigma$  bond. From this observation, theoretical calculations present a similar correlation for the resonant and off-resonant molecular hyperpolarizabilities  $\beta_{xxx}$  and  $\beta_{xxx,0}$  respectively.

In an effort to confirm the effect of the *N*-Boc substituent, cation **6d** was also calculated without the protecting group (**6d'** system) as all attempts to deprotect this compound were unsuccessful. For cation **6d'** the maximum absorption is 330 nm, the HRS hyperpolarizability is  $32 \times 10^{-30}$  esu and the resonance and off-resonance diagonal components of the molecular hyperpolarizability are  $-75 \times 10^{-30}$  esu and  $-35 \times 10^{-30}$  esu, respectively. These values were obtained under the same theoretical conditions as the results in Table 4. It can be seen that the optical properties  $\lambda_{\max}$  and  $\beta_{\text{HRS}}$  are not affected by the presence of the *N*-Boc substituent on the donor fragment. A similar conclusion can be drawn from the diagonal components of the molecular hyperpolarizabilities. The opposite sign is related to the change in the relative orientation between dipole moment and hyperpolarizability vectors of cation **6d'** with respect to that of the **6d** system.

## Conclusions

In summary, the synthesis of push-pull molecules combining heteroaromatic cations as acceptor units (A<sup>+</sup>) with  $\pi$ -excessive *N*-heterocycles as donor units (D), with a  $\sigma$  bond connecting the units, was achieved by Stille cross-coupling reactions.

The first hyperpolarizabilities ( $\beta_{\text{HRS}}$ ) of the series of charged chromophores show that chromophore **6b** having indole as a donor unit has a significantly higher value than the rest of the synthesized cationic systems. The low transition energy and high level of CT are the decisive factors that provide a higher first hyperpolarizability in compounds substituted at C4. Theoretical calculations support the experimental results and also predict the largest  $\beta_{\text{HRS}}$  value for **6b**.

In comparison to previously reported (D- $\pi$ -A<sup>+</sup>) molecules<sup>13a</sup> the lack of a conjugated bridge in these (D-A<sup>+</sup>) chromophores does not seem to be significant in terms of higher  $\beta_{\text{HRS}}$  values, with the magnitude of  $\beta$  in this kind of chromophore being dominated by additive contributions from the donors and the acceptors. The results may prove useful in guiding the design of new NLO materials, contributing to the recent interest in  $\beta$  enhancement strategies.<sup>23</sup>

## Experimental section

### General procedure for the synthesis of D-A pyridinium salts

A dry flask was charged under argon with 1 equiv. of bromopyridinium iodide or hexafluorophosphate; 5 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0333 mmol, 0.0384 g) (*Method A*) or 5 mol% Pd<sub>2</sub>(dba)<sub>3</sub>

(0.0333 mmol, 0.0305 g) and 5 mol% P(*o*-Tol)<sub>3</sub> (*Method B*) in dry DMF (10 mL). 2.1 equiv. of the corresponding stannyl heterocycle (1.3213 mmol) were added to the reaction. The mixture was stirred at 65 °C for 15–20 h and the solution was filtered through a small pad of Celite and washed with methanol. The solution was concentrated and the solids were purified by flash chromatography on silica gel, with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (9 : 1) as an eluent, to give **4**, **5** and **6**.

**1-Methyl-4-(1H-pyrrol-3-yl)pyridinium iodide (4a).** General procedure B gave 0.0381 g (13%) of product as a brown dusty solid: mp 142–144 °C; IR (KBr) 3445; 3031; 1488; 664 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD) 9.27 (s, 1H); 8.72 (d, 1H, *J* = 8.1); 8.60 (d, 1H, *J* = 6.2); 7.98 (t, 1H, *J* = 6.2); 7.73–7.71 (m, 1H); 7.04–7.01 (m, 1H); 6.90–6.88 (m, 1H); 4.46 (s, 3H); <sup>13</sup>C NMR (75 MHz, acetone)  $\delta$  142.2; 141.6; 139.9; 137.6; 128.4; 127.5; 126.3; 120.5; 109.6; 48.8. MS (ES<sup>+</sup>) *m/z* (relative intensity) 159 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>I: C 41.96; H: 3.85; N: 9.79. Found: C, 41.93; H, 3.90; N, 9.80.

**1-Methyl-3-(1H-indol-3-yl)pyridinium iodide (4b).** General procedure A gave 0.0381 g (51%) of product as a brown solid: mp 290 °C; IR (KBr) 3416, 3178.76 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD): 9.24 (s, 1H); 8.88 (d, 1H, *J* = 8.4); 8.67 (d, 1H, *J* = 5.9); 8.04 (t, 1H, *J* = 4.7); 8.0 (s, 1H); 7.58–7.54 (m, 2H); 7.33–7.28 (m, 2H); 4.5 (s, 3H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) 142.9; 141.7; 138.8; 128.9; 127.5; 125.5; 124.0; 122.4; 119.5; 113.4; 110.3; MS (ES<sup>+</sup>) *m/z* (relative intensity) 209 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>I: C 50.02; H 3.87; N 8.33. Found: C 49.94; H 3.90; N 8.33.

**1-Methyl-3-(1-trityl-1H-pyrazol-4-yl)pyridinium iodide (4c).** General procedure A gave 0.0667 g (53%) of product as a brown solid: mp 246 °C; IR (KBr) 3419, 3055, 1631, 1373 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD) 9.25 (s, 1H); 8.74–8.69 (m, 2H); 8.27 (s, 2H); 8.01 (t, 1H, *J* = 6.2); 7.41–7.38 (m, 9H); 7.24–7.19 (m, 6H); 4.41 (s, 3H); <sup>13</sup>C NMR (75 MHz, acetone)  $\delta$  143.7; 143.1; 141.4; 138.5; 134.6; 132.4; 130.9; 128.8; 128.8; 128.7; 115.9; 73.0; 61.7; 49.1. MS (ES<sup>+</sup>) *m/z* (relative intensity) 402 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>28</sub>H<sub>24</sub>N<sub>3</sub>I: C 63.52; H 4.54; N 7.94. Found: C 62.93; H 3.71; N 7.25.

**1-Methyl-3-(1H-indazol-3-yl)pyridinium iodide (4d).** General procedure A gave 0.0927 g (33%) of a brown solid: mp 158–160 °C; IR (KBr) 3133, 1633, 1588, 1172 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD): 9.54 (s, 1H); 9.19 (d, 1H, *J* = 8.0); 8.90 (d, 1H, *J* = 5.8); 8.28–8.19 (m, 2H); 7.71 (d, 1H, *J* = 8.4); 7.55 (t, 1H, *J* = 8.0); 7.40 (t, 1H, *J* = 7.5); 4.58 (s, 3H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) 146.1; 132.7; 131.5; 131.3; 128.2; 127.7; 127.5; 127.1; 124.8; MS (ES<sup>+</sup>) *m/z* (relative intensity) 210 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>I: C 46.29; H 3.56; N 12.46. Found: C 46.21; H 3.44; N: 11.65.

**1-Methyl-2-(1-trityl-1H-pyrazol-4-yl)pyridinium iodide (5c).** General procedure A gave 0.0123 g (34%) of an orange solid: mp 249–250 °C; IR (KBr) 3428, 2920, 1625, 1382 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD): 8.89 (d, 1H, *J* = 6.2); 8.48 (t, 1H, *J* = 7.5); 8.24 (s, 1H); 8.21 (s, 1H); 8.17 (d, 1H, *J* = 8.4); 7.92 (t, 1H, *J* = 7.0); 7.43–7.40 (m, 9H); 7.27–7.22 (m, 6H); 4.36 (s, 3H); <sup>13</sup>C NMR (75 MHz, DMSO): 145.6; 143.8; 141.4; 139.7; 134.5; 129.0; 128.3; 127.4; 124.4; 111.9; 78.6; 46.7. MS (ES<sup>+</sup>) *m/z* (relative



intensity) 402 ( $M^+$ , 100). Anal. Calcd for  $C_{28}H_{24}N_3I$ : C, 63.41; H, 4.71; N, 7.93. Found: C 63.43; H 4.74; N 7.95.

**1-Methyl-2-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-yl)pyridinium iodide (5d).** General procedure A gave 0.035 g (31%) of an orange oil; IR (KBr) 3133, 1634, 1589, 1172  $cm^{-1}$ ;  $^1H$  NMR (200 MHz,  $CD_3OD$ ): 9.10 (d, 1H,  $J = 6.2$ ); 8.65 (t, 1H,  $J = 8.1$ ); 8.10 (t, 2H,  $J = 6.2$ ); 8.00 (d, 1H,  $J = 7.7$ ); 7.83 (d, 1H,  $J = 7.7$ ); 7.67 (t, 2H,  $J = 7.9$ ); 4.91 (s, 3H); 1.57 (s, 9H).  $^{13}C$  NMR (75 MHz,  $CD_3OD$ ): 152.0; 145.0; 143.8; 135.7; 135.0; 131.2; 129.5; 129.2; 128.2; 122.0; 116.6; 114.7; 111.7; 72.0, 49.0; 45.5. MS ( $ES^+$ )  $m/z$  (relative intensity) 310 ( $M^+$ , 100). Anal. Calcd for  $C_{18}H_{20}N_3O_2I$ : C 49.44; H 4.58; N 9.61. Found: C 49.2; H 4.44; N 9.65.

**1-Methyl-4-(1*H*-pyrrol-3-yl)pyridinium hexafluorophosphate (6a).** Procedure B gave a brown solid (0.2917 g, 98%): mp 106–108 °C; IR (KBr) 3420, 3199, 1638  $cm^{-1}$ ;  $^1H$  NMR (200 MHz,  $CD_3OD$ ) 8.52 (d, 2H,  $J = 6.9$ ); 8.07 (d, 2H,  $J = 6.9$ ); 7.84 (s, 1H); 7.00–6.98 (m, 1H); 6.85–6.82 (m, 1H), 4.23 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ )  $\delta$  145.2; 128.2; 125.7; 122.9; 121.9; 109.6; 108.2; 47.7. MS ( $ES^+$ )  $m/z$  (relative intensity) 159 ( $M^+$ , 100). Anal. Calcd for  $C_{10}H_{11}N_2PF_6$ : C 69.08; H 3.62; N 9.21. Found: C 69.24; H 3.50; N 9.33.

**1-Methyl-4-(1*H*-indol-3-yl)pyridinium hexafluorophosphate (6b).** Procedure A, brown solid (0.2917 g, 78%): mp 222 °C; IR (KBr) 3414, 1645, 1557, 836  $cm^{-1}$ ;  $^1H$  NMR (200 MHz,  $CD_3OD$ ): 8.56 (d, 2H,  $J = 7.3$ ); 8.38 (s, 1H); 8.30 (d, 2H,  $J = 6.9$ ); 8.16–8.12 (m, 1H); 7.61–7.57 (m, 1H), 7.40–7.34 (m, 2H); 4.26 (s, 3H).  $^{13}C$  NMR (75 MHz,  $CD_3OD$ ) 145.1; 132.4; 124.6; 123.6; 122.5; 121.5; 120.5; 113.9; 47.7. MS ( $ES^+$ )  $m/z$  (relative intensity) 209 ( $M^+$ , 100). Anal. Calcd for  $C_{14}H_{13}N_2PF_6$ : C 47.46; H 3.67; N 7.91. Found: C 47.33; H 3.52; N 8.02.

**1-Methyl-4-(1-trityl-1*H*-pyrazol-4-yl)pyridinium hexafluorophosphate (6c).** General procedure A gave 0.3203 g (91%) of a yellow solid: mp 204–206 °C; IR (KBr) 3431, 3134, 1640, 1385  $cm^{-1}$ ;  $^1H$  NMR (200 MHz,  $CD_3OD$ ) 8.65 (d, 2H,  $J = 6.6$ ); 8.43 (s, 1H); 8.42 (s, 1H); 8.18 (d, 2H,  $J = 6.7$ ); 7.41–7.39 (m, 9H), 7.23–7.20 (m, 6H); 4.30 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ )  $\delta$  147.1; 144.5; 141.6; 138.9; 133.3; 129.1; 127.6; 127.5; 127.4; 121.6; 116.4; 78.7; 46.1. MS ( $ES^+$ )  $m/z$  (relative intensity) 402 ( $M^+$ , 100). Anal. Calcd for  $C_{28}H_{24}N_3PF_6$ : C 61.43; H 4.39; N 7.68. Found: C, 61.05; H, 3.95; N, 6.85.

**1-Methyl-4-(1-*tert*-butoxycarbonyl-1*H*-indazol-3-yl)pyridinium hexafluorophosphate (6d).** General procedure A gave 0.296 g (90%) of an orange solid: mp 119–121 °C; IR (KBr) 3413, 1644, 1265, 834.49  $cm^{-1}$ ;  $^1H$  NMR (200 MHz, acetone): 9.10 (d, 2H,  $J = 6.3$ ); 8.73 (d, 2H,  $J = 6.3$ ); 8.38 (d, 1H,  $J = 8.4$ ); 8.25 (d, 1H,  $J = 7.4$ ); 7.78 (t, 1H,  $J = 8.5$ ); 7.60 (t, 1H,  $J = 7.3$ ); 4.41 (s, 3H); 1.70 (s, 9H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ ): 147.3; 145.6; 142.4; 140.2; 129.5; 124.9; 124.5; 122.3; 120.7; 114.3; 85.6; 47.2. MS ( $ES^+$ )  $m/z$  (relative intensity) 310 ( $M^+$ , 100). Anal. Calcd for  $C_{18}H_{20}N_3O_2PF_6$ : C 47.47; H 4.40; N 9.23. Found: C 47.63; H 4.23; N 9.10.

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