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## Heteroaromatic Cation-Based Chromophores: Synthesis and Nonlinear Optical **Properties of Alkynylazinium Salts**

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A variety of alkynylazinium cationic (D- $\pi$ -A<sup>+</sup>) chromophores were prepared in good yields by the reaction of bromoazinium (pyridinium, quinolinium, and isoquinolinium iodides) with alkynes under Sonogashira conditions. The analysis of the experimentally recorded spectra is supported by quantum chemical calculations using restricted configuration interaction and density functional methods. First-order hyperpolarizabilities of  $(D-\pi-A^+)$  azinium-based cations as a new class of second-order nonlinear optical (NLO) chromophores were also studied by hyper-Rayleigh scattering experiments and computational procedures.

## Introduction

Most organic compounds with nonlinear optical (NLO) properties are based on highly conjugated molecules with donors and acceptors substituted at the two ends of the molecule. These donor-acceptor ("push-pull") systems are amongst the most interesting structures for new compounds with efficient NLO responses.<sup>[1]</sup> In these systems, particular effort has been made to find the optimum combination of the bridge, acceptor and donor groups with the aim of enhancing the NLO response, particularly with molecules that can be chemically fine-tuned for desired applications.<sup>[2]</sup>

In this context, organic chromophores containing different acceptor units, such as nitro,<sup>[3]</sup> nitrile,<sup>[4]</sup> sulfonyl,<sup>[5]</sup> polycyanoviny1<sup>[6]</sup> and phosphonate<sup>[7]</sup> salts, inter alia, have been explored previously. The use of charged moieties as acceptor units is restricted to diazonium salts<sup>[8]</sup> and some heteroaromatic cations; for example, benzothiazolium<sup>[9]</sup> and pyridinium salts<sup>[10]</sup> have been studied as cationic and dicationic acceptors in a few push-pull systems such as those shown in Figure 1.

Our research findings in the development of the chemistry of heteroaromatic cations<sup>[11]</sup> led us to undertake a comparative study in which different azinium (pyridinium, quinolinium and isoquinolinium), azolium (imidazolium and

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Figure 1. Examples of D-π-A<sup>+</sup> NLO-phores based on heteroaromatic cation-acceptor units.

benzimidazolium) and azonia (quinolizinium and aza-quinolizinium) cations were studied as potential acceptor units in a variety of NLO-catiophores. We report here our initial results on the synthesis of a series of charged chromophores, D-\u03c0-A<sup>+</sup> (Figure 2), by Sonogashira<sup>[12]</sup> cross-cou-





Figure 2. General structure of donor-acceptor molecules based on azinium heteroaromatic cations.

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pling reactions. The basic strategy for the construction of push-pull molecules is to combine charged heteroaromatic cations – employed as acceptor units  $(A^+)$  – with donor

units (D) through a  $\pi$ -bridge. The resulting D- $\pi$ -A+ chromophores, which bear electron-donating substituents on the benzene ring, were studied by hyper-Rayleigh scattering ex-

Table 1. Sonogashira reaction on bromo-1-methylpyridinium iodides 1a-c.



[a] Yields refer to isolated yields. [b] Dehalogenation. [c] Starting material.



periments.<sup>[13]</sup> Other chromophores were also considered for comparative purposes in order to gain an understanding of the observed NLO properties. Furthermore, the experimental study is supported by a theoretical analysis combining a variety of computational procedures, including Density Funtional Theory (DFT) and correlated Hartree–Fockbased methods [RCIS(D)].

## **Results and Discussion**

The first series of pyridinium-based chromophores was obtained from 3-bromo- (1a), 2-bromo- (1b), and 4-bromo-1-methylpyridinium iodide (1c), which were coupled with different alkynes under Sonogashira conditions.<sup>[13]</sup> The salt 1a, which was the least reactive substrate compared with 1b and 1c, was initially used as a model compound to determine the best conditions for the reaction with triisopropylsilylacetylene (TIPS). The best conditions found involved the use of Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol-%), CuI (10 mol-%) and Et<sub>3</sub>N (1.5 equiv.) in DMF at room temperature. Under these conditions, triisopropylsilylacetylene (1.2 equiv.) gave **2a** in 75% yield (Table 1, Entry 1) after exchange of the iodide counterion by hexafluorophosphate in order to facilitate the isolation of the product.<sup>[14]</sup> In light of this success, the same conditions were used to treat 3-bromopyridinium iodide with different arylacetylenes to give the coupling products (Table 1) in yields of up to 49%.

The differences in yield are probably due to the purification process rather than to electronic effects associated with the coupling partners. Thus, the best yields were obtained for **2a** and **2b** as the  $PF_6^-$  salt. For the rest of the reactions, leading to **2c**–**f**, better yields were obtained when the products were isolated as iodides. It is worth noting that compound **2f** was obtained in a better yield than expected for a system with an electron-withdrawing substituent on the benzene ring (Table 1, Entry 6).

Next, we examined the reactivity at the C-2 and C-4 positions of the pyridinium ring with substrates **1b**,**c** under the optimal conditions found for **1a**. In general, yields of the coupled compounds were lower than for **2a**. In an analo-

Table 2. Sonogashira coupling on 3- and and 4-bromo-1-methylisoquinolinium salts 1d-e.



[a] Yields refer to isolated yields. [b] Starting material + homocoupling product. [c] Decomposition.

gous way to reactions with **1a**, better yields were obtained when the coupling products were isolated as iodides, except for **3a**. The main difference in the reactivity of **1a** and **1b** was observed in their reactions with 2-pyridylacetylene, which in the case of **1b** gave the dehalogenated pyridinium salt as the main product. All attempts to overcome the dehalogenation process, and the concomitant formation of the 1-methylpyridinium salt, proved unsuccessful.

The yields of coupled products obtained from 1c, as hexafluorophosphates in all cases (Table 1), were in the range 45–66%. In this case, the reaction with 2-ethynylpyridine was also unsuccessful, affording a complex reaction mixture along with the dehalogenated starting material and 1c as the main compounds. These unsuccessful results can be explained in terms of the higher stabilization of  $\alpha$ - and  $\gamma$ -ylides formed in the dehalogenation process when compared to the less stable  $\beta$ -ylide, formed in the dehalogenation of 1a.

Having demonstrated that salts **1a–c** can act as efficient partners in Sonogashira reactions, we extended the reaction to quinolinium and isoquinolinium derivatives. Thus, 3bromo-1-methylquinolinium iodide (**1d**) and 4-bromo-2methylisoquinolinium iodide (**1e**) reacted with certain acetylenes to afford the coupling products **5** and **6** in moderate or low yields (Table 2).

In both cases the reaction with 2-pyridylacetylene failed to give the coupled product. Moreover, **1e** seemed to be less reactive with all the acetylenes tested, and the reaction was also unsuccessful with 1-ethynyl-4-(trifluoromethyl)benzene, which gave a complex reaction mixture. An NMR study of the reaction mixtures allowed the identification of the homocoupling product of **1e**.

A comparative study of linear and non-linear optical properties of chromophores was carried out on a selection of the chromophores shown in Tables 1 and 2. A range of systems bearing electron-donating substituents on the benzene ring were considered, although whenever possible, chromophores bearing electron-withdrawing substituents were also considered for comparative purposes. Selected compounds are shown in Figure 3.



Figure 3. Selected chromophores for the study of linear and non-linear optical properties.

#### **Linear Optical Properties**

The absorption spectra of the selected chromophores were recorded in the range 200–1000 nm. The absorption spectra for a group of representative molecules [2c, 3c and 4c in (a); 5b and 6b in (b)] are shown in Figure 4. The compounds did not show any absorption above 450 nm.

In general, a good correlation was found between the electron-donating substituents used and the stabilization energy for all the different types of chromophores: the bromophenyl substituent is the weakest donor and, as expected, yielded the smalles  $\lambda_{max}$  value; the tolyl substituent



Figure 4. Absorption and emission spectra for some selected chromophores (in methanol at 25 °C). Fluorescence quantum yields and lifetime averages are superimposed.



is an intermediate donor and yielded an intermediate  $\lambda_{max}$  value; the methoxyphenyl substituent is the best donor, yielding the largest  $\lambda_{max}$  value. A good correlation was also found for all compounds between the position of the pyridinium nitrogen atom and the wavelength of the absorption maximum: a nitrogen atom in the  $\gamma$ -position resulted in the most efficient conjugation, whereas a nitrogen atom in the  $\beta$ -position resulted in a less efficient conjugation. The effects of the  $\alpha$ -position varied from group to group, but in general the efficiency of the conjugation was somewhere between the effects of the  $\gamma$ - and the  $\beta$ -positions, probably due to a combination of electronic and steric effects.

The use of different electron-donating/withdrawing substituents also affects the stabilization energy of the chromophores. A bathochromic effect is exerted on the absorption spectrum of chromophores bearing electron-donating substituents in comparison to those containing electron-withdrawing ones. Thus, the maximum of the  $\pi$ - $\pi$ \* absorption bands for compounds containing methoxy substituents is shifted towards longer wavelengths by approximately 30– 40 nm with respect to those containing bromo substituents. Comparison of the absorption maxima (data collected in Table 3) and/or the spectra for compounds **2c**, **3c** and **4c**, which contain the same electron-donating methoxy group at a different location with respect to the pyridinium nitrogen atom, reveals a better stabilization when the substituent is at the  $\alpha$ -position compared to the  $\gamma$ - and  $\beta$ -positions.

Table 3. Nonlinear optical properties of selected chromophores 2-6 shown in Figure 3.<sup>[a]</sup>

Compound	λ <sub>max</sub>	$\beta_{\rm HRS}$	$\beta_{zzz}$	$\beta_{zzz,0}$	τ
2b	<300	_	_	_	_
3b	344	$140 \pm 10$	$350 \pm 30$	$74 \pm 7$	$5\pm 2$
4b	342	$55 \pm 2$	$135 \pm 5$	$29 \pm 1$	$4\pm1$
5b	379	$230 \pm 20$	$550 \pm 60$	$44 \pm 5$	_
6b	370	$92 \pm 9$	$220 \pm 20$	$25 \pm 2$	_
2c	362	$176 \pm 7$	$430 \pm 20$	$61 \pm 2$	_
3c	360	$129 \pm 4$	$312 \pm 10$	$47 \pm 2$	_
4c	370	$210 \pm 10$	$500 \pm 30$	$56 \pm 3$	_
2f	<300	$25 \pm 2$	$60 \pm 5$	—x-	_
3f	331	$40\pm8$	$100 \pm 20$	$25 \pm 4$	_
<b>4f</b>	331	$28 \pm 2$	$68 \pm 5$	$18 \pm 2$	_

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

Replacement of the pyridinium acceptor in **2c**, **3c** or **4c** by quinolinium (**5b**) or isoquinolinium (**6b**) results in a bathochromic shift and a significant decrease in the intensity of the low-energy absorption band.

Fluorescence emission for 2, 3 and 4, obtained upon excitation at the wavelength of the  $\pi$ - $\pi$ \* band, exhibits features similar to those of the absorption spectra. The substituent groups that contribute to the stability of the systems by extending the conjugation show emission at longer wavelengths. For example, the fluorescence maxima for 3c and 4c are located at approximately 579 and 594 nm, whereas for **2c** the maximum is at 537 nm. The emission spectra of **5b** and **6b** are significantly different, with maxima at 447 and 546, respectively. The fluorescence quantum yields ( $\Phi$ f) and intensity decay profiles for all of the systems were characterized in methanol at 25 °C (superimposed in Figure 4 and/or included in the Supporting Information). In general, most of the samples exhibit  $\Phi$ f < 0.1. Strong donor/acceptor groups usually lead to efficient transfer, such as HOMO–LUMO transitions, and fluorescence is subsequently quenched in relatively polar solvents.<sup>[15]</sup> Fluorescence intensity profiles for all the samples fitted to bi-exponential decays.

# Nonlinear Optical Properties – Hyper-Rayleigh Scattering (HRS) Studies

Femtosecond hyper-Rayleigh scattering measurements performed at 800 nm on selected compounds are compiled in Table 3. Congruent with the trends already observed in the linear optical (absorption) experiments, the first hyperpolarizability value for the compounds with a pyridinium acceptor increases when the methoxyphenyl group is present as the aryl donor (**2c**, **3c** and **4c**), and the most marked effect is seen when the pyridinium nitrogen atom is in the  $\gamma$ -position (**4c**). The value for the first hyperpolarizability of this group of compounds compares favorably with values for other short chromophores,<sup>[9,10a,10c,10d,10g]</sup> with absorption maxima trending to longer wavelengths. This trend, however, has not been confirmed in the isoquinolinium derivatives.

#### **Theoretical Studies**

Depending on the spectroscopic property under study, different theoretical methodologies have been used. The relatively large size of the studied systems places most of the ab initio techniques outside the area of applicability. The configuration interaction with single- and double-excitation methods [CIS(D)] as well as time-dependent density functional theory (TDDFT) seem to be the most popular approaches for the calculation of excitation spectra. All theoretical calculations were performed by using the Gaussian suite of quantum chemical programs.<sup>[16]</sup> For all the studied cationic systems, the molecular structure used to compute the nonlinear optical properties correspond to a minimum energy calculated at the HF/6-31G(d) level. These structures have been checked to be minima by evaluation of the harmonic vibrational frequencies, which were all real.

For the first excited state of the studied cationic systems, the calculated wavelengths have been compared to the experimentally determined ( $\lambda_{max}$  [nm]). These wavelengths have been estimated from two different approaches: (i) The CIS(D)<sup>[17]</sup> method, which generally predicts accurately excited states that are mainly one-electron transitions from a single reference ground state; (ii) the CAM-B3LYP<sup>[18]</sup> functional density, recently developed to account for long-range interactions (Table 4).

Table 4. Wavelengths ( $\lambda_{max}$  [nm]) of absorption maxima determined experimentally and theoretically calculated at the CIS(D)/6-31G(d) and CAM-B3LYP/6-31G(d) levels of theory.

Compound	$\lambda_{\max} \exp$ .	CIS(D)	CAM-B3LYP
2b	<300	289	359
3b	344	311	349
4b	342	336	363
5b	379	377	394
6b	370	343	400
2c	362	325	389
3c	360	342	371
4c	370	374	386
2f	<300	267	355
3f	331	290	352
<b>4</b> f	331	310	367

Table 4 shows a comparison between experimentally observed and theoretically predicted wavelengths for the first excited electronic state. The CIS(D)-calculated wavelengths are underestimated with respect to the experimental values. For the selected systems, the largest deviation from the experimental value is about 10%. The predicted values for systems 2b and 2f are clearly smaller than 300 nm, in accordance with the experimental measurements. In the particular case of **5b**, the experimental value of  $\lambda_{max}$  is in very good agreement with the theoretical result. On the other hand, the wavelengths at the CAM-B3LYP level are overestimated with respect to the experimental values by about 5-10%. CAM-B3LYP calculations predict the existence of a second more intense peak at 339 nm for 2c as a result of a HOMO $\rightarrow$ LUMO+1 transition. For **5b**, the theoretical value of 394 nm obtained by using the CAM-B3LYP functional also corresponds to a HOMO $\rightarrow$ LUMO+1 transition. With these exceptions, all the studied compounds have an intense HOMO-LUMO transition leading to an efficient charge transfer between donor and acceptor moieties. This can be seen in Figure 5, where the main contributions to the HOMO and LUMO are due to the donor and acceptor fragments, respectively. For both theoretical methodologies, calculated  $\lambda_{max}$  values for the methoxyphenyl substituents (2c, 3c and 4c) present the largest values, as expected for the best donors. The weaker donors - the bromophenyl substituents (2f, 3f and 4f) – show the smallest  $\lambda_{max}$  values, and the bathochromic shift of the quinolinium and isoquinolinium (5b and 6b)  $\lambda_{max}$  values with respect to the pyridinium acceptors is also reproduced.



Figure 5. HOMO (a) and LUMO (b) of 4c.

A. M. Cuadro, J. J. Vaquero et al.

Theoretical estimation of the second harmonic generation (SHG) of hyperpolarizability  $\beta(-2\omega;\omega,\omega)$  was also performed. This theoretical value has been compared to  $\beta_{\text{HRS}}$ , which is experimentally determined by hyper-Rayleigh scattering (HRS) for cationic systems. The resonant or frequency-dependent hyperpolarizabilities obtained by calculations at the MP2/6-31G(d) level of theory include the electron-correlation effect in this NLO property  $\beta_{\text{MP2}}(-2\omega;\omega,\omega)$ . This property has been estimated from the resonant or dynamic  $\beta(-2\omega;\omega,\omega)$  at the HF/6-31G(d) level, and the static or nonresonant value  $\beta(0;0,0)$ , 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 [Equation (1)].<sup>[19]</sup>

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

The first hyperpolarizability  $\beta$  has been calculated as a second dipole moment derivative with respect to electric fields. At the Hartree–Fock (HF) level, these dipole derivatives are calculated analytically by solving the corresponding CPHF equations. On the other hand, when the electron-correlation effect has been included by means of the perturbative MP2 approach, these dipole derivatives are obtained numerically. Calculated hyperpolarizabilities are obtained in the molecular axes  $\beta_{ijk}$  and then transformed to the laboratory axes  $\beta_{XYZ}$  by applying the Civin et al. expressions published elsewhere.<sup>[20]</sup>

In Table 5, two different kinds of data are presented: HRS hyperpolarizabilities and dispersion. Although calculated  $\beta_{\text{HRS}}$  values did not qualitatively reproduce the observed values, the larger  $\beta_{\text{HRS}}$  values are obtained when methoxyphenyl substituents are the donors (**2c**, **3c** and **4c**) with pyridinium acceptors. This is the most important effect in cation **4c**, in good agreement with the experimental data. Dispersion  $\rho$  has a value of 5 in the limit of pure linear molecules, as can be seen from the Civin et al. expressions. It is sensitive to the different contributions of the nonzero  $\beta$  tensor components, and therefore to the symmetry of the scatterer. The calculated dispersion values  $\rho$  at 800 nm for these cations are between 4.8 and 5.3, as it should be for

Table 5. Resonance-enhanced HRS experimental first hyperpolarizability  $\beta_{\rm HRS}$ , the MP2/6-31G(d) calculations of  $\beta_{\rm HRS}$  at 800 nm, and dispersion  $\rho$  at 400 nm ( $\beta_{\rm HRS}$  values are given in 10<sup>-30</sup> esu).

Compound	$\beta_{\rm HRS}$		ρ
	Exp	800 nm	400 nm
2b	_	53	2.5
3b	140	77	4.2
<b>4b</b>	55	139	3.8
5b	230	108	2.4
6b	92	102	2.5
2c	176	88	4.4
3c	129	130	2.9
4c	210	234	2.5
2f	25	34	5.3
3f	40	48	2.4
<b>4</b> f	28	85	3.6

these systems. On the other hand, at 400 nm the calculated dispersion values are quite different, as shown in Table 5. These changes can be due to the resonance between the optical frequency and the  $\lambda_{max}$  absorption, or to changes induced in the electronic cloud for the optical frequency, or both. They could probably explain the disagreement between calculated and observed HRS hyperpolarizabilities.

### Conclusions

The synthesis of a series of  $D-\pi$ -A<sup>+</sup> catiophores was achieved by Sonogashira cross-coupling reactions of azinium bromo derivatives. This process gave moderate to good yields, and had a simple workup procedure. The first hyperpolarizability values for this group of compounds compare favourably with those of other short chromophores. It is clear from this study that D-A systems containing the *p*-methoxyphenyl donor and the pyridinium acceptor show the largest second-order nonlinearity. Further variations in the type of D/A<sup>+</sup> groups should allow higher values to be obtained.

### **Experimental Section**

# General Procedure for the Preparation of *N*-Methylazinium Salts 2–6

**General Procedure A:** A flame-dried round-bottomed flask (10 mL) was charged under argon with the corresponding pyridinium salt (100 mg, 0.3335 mmol), 10 mol-% of CuI (6.35 mg, 0.0333 mmol) and 5 mol-% of Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (11.7 mg, 0.0167 mmol) in dry DMF (5 mL). The corresponding acetylene (0.4002 mmol, 1.2 equiv.) and dry Et<sub>3</sub>N (87  $\mu$ L, 0.5003 mmol, 1.5 equiv.) were added, and the reaction mixture was stirred at room temperature as indicated. The reaction mixture was concentrated under reduced pressure, and the residue was treated with saturated aqueous NH<sub>4</sub>PF<sub>6</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated under reduced pressure, and the product was purified by flash chromatography on silica gel by using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (different proportions) as eluent or by treatment with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (8:2).

**1-Methyl-3-[(triisopropylsilyl)ethynyl]pyridinium** Hexafluorophosphate (2a): According to General Procedure A, from 1a and (triisopropylsilyl)acetylene (89.8 μL, 0.4002 mmol). The reaction mixture was stirred for 24 h, and the crude product was purified by flash chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (9.5:0.5) as the eluent. Product **2a** (88.3 mg, 75%) was obtained as a brown solid, m.p. 89–90 °C. IR (KBr):  $\tilde{v}_{max}$  = 3125, 2944, 2868, 1506, 1466, 831 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD):  $\delta$  = 9.34 (s, 1 H, Ar-H), 9.10 (d, *J* = 6.4 Hz, 1 H, Ar-H), 8.76 (d, *J* = 8.0 Hz, 1 H, Ar-H), 8.26 (dd, *J* = 6.4, 8.0 Hz, 1 H, Ar-H), 4.64 (s, 3 H, N-CH<sub>3</sub>), 1.14 {m, 21 H, Si-[CH(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>} ppm.<sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD):  $\delta$  = 147.6, 146.3, 144.5, 127.1, 121.7, 98.9, 98.7, 47.6, 17.9, 10.1 ppm. MS (ES<sup>+</sup>): *m/z* (%) = 275 (100) [M<sup>+</sup>]. C<sub>17</sub>H<sub>28</sub>NSi·F<sub>6</sub>P (419.16): calcd. C 48.68, H 6.73, N 3.34; found C 50.00, H 6.66, N 3.20.

**General Procedure B:** A flame-dried round-bottomed flask (10 mL) was charged under argon with the corresponding pyridinium salt (100 mg, 0.3335 mmol), 10 mol-% of CuI (6.35 mg, 0.0333 mmol) and 5 mol-% of  $Pd_2Cl_2(PPh_3)_2$  (11.7 mg, 0.0167 mmol) in dry DMF (5 mL). The corresponding acetylene (0.4002 mmol) and dry  $Et_3N$ 



(87  $\mu$ L, 0.5003 mmol) were added, and the reaction mixture was stirred at room temperature as indicated. The reaction mixture was concentrated under reduced pressure, the residue was treated with saturated aqueous NaHCO<sub>3</sub> (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and purified by treatment with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (8:2).

**1-Methyl-3-{***[p*-(trifluoromethyl)phenyl]ethynyl}pyridinium Iodide (2d): Compound 1a and 1-ethynyl-4-(trifluoromethyl)benzene (57.0 μL, 0.4002 mmol) were allowed to react according to the General Procedure B by stirring the reaction mixture for 3.5 h to give 2d (82.4 mg, 69%) as a white solid, m.p. 187–189 °C. IR (KBr):  $\tilde{v}_{max} = 3135, 2230, 1636, 1327 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta = 9.42$  (s, 1 H, Ar-H), 9.15 (d, J = 6.2 Hz, 1 H, Ar-H), 8.85 (d, J = 10.2 Hz, 1 H, Ar-H), 8.33 (dd, J = 8.0, 6.2 Hz, 1 H, Ar-H), 7.86 (s, 4 H, Ar-H), 4.70 (s, 3 H, N-CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (50 MHz, DMSO):  $\delta = 148.7, 147.2, 146.0, 133.3, 130.7$  (q, J = 32.7 Hz), 128.4, 126.7 (q, J = 3.2 Hz), 125.3, 124.5 (q, J = 286.7 Hz), 122.7, 94.7, 85.4, 46.5 ppm. MS (ES<sup>+</sup>): m/z (%) = 262 (100) [M<sup>+</sup>]. C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N·I (388.98): calcd. C 53.59, H 4.50, N 4.17; found C 53.54, H 4.39, N 4.25.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic characterization data of all new compounds (2b-c, 2e-f; 3a-d, 3f; 4a-d, 4f; 5a-c; 6a-b), tables of quantum yields and absorption spectra for 2-4b and 2-4f.

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