

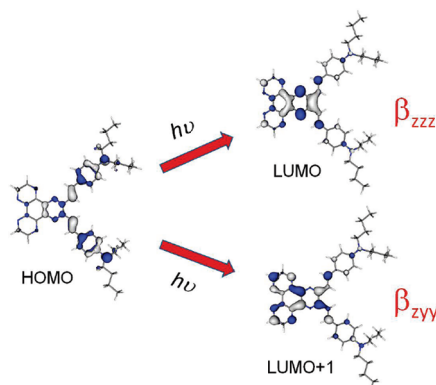
## Synthesis and Electrochemical and Theoretical Studies of V-Shaped Donor–Acceptor Hexaazatriphenylene Derivatives for Second Harmonic Generation

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In this article we describe novel synthetic strategies toward well-defined disubstituted conjugated hexaazatriphenylene (HAT) derivatives. The systems are designed as novel V-shaped chromophores displaying  $C_2$  symmetry suitable for nonlinear optical investigations. Different donor moieties and linkers have been used in order to tune the electrochemical properties as well as the absorption spectra of the novel HAT derivatives.  $\mu\beta$  values as high as  $1010 \times 10^{-48}$  esu have been obtained for a derivative containing the electron-rich dibutyl-amino moiety. Theoretical calculations have been performed showing a reasonable agreement with the experimental results and supporting the two-dimensional NLO character of these chromophores.

### 1. Introduction

1,4,5,8,9,12-Hexaazatriphenylene (HAT) was first synthesized in 1981<sup>1</sup> as a novel metal ligand for coordination chemistry. The six nitrogen atoms allow HAT to act as a triple bidentate ligand that can bond up to three metal atoms. This property has been widely used for the construction of metal–organic frameworks of different complexity.<sup>2</sup> The photophysical and photochemical properties of some HAT complexes have also demanded interest today due to their capability of interaction

with DNA in different ways.<sup>3,4</sup> Although most of the literature concerned with the HAT system deals with its coordination properties and the properties of the corresponding complexes, in the last years some work has also been done to study its properties and applications in the absence of metals.

Theoretical investigations have been reported<sup>5–7</sup> as well as numerous contributions involving experimental properties

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like liquid crystal behavior,<sup>8–16</sup> electron mobility,<sup>17–20</sup> self-assembly,<sup>21–28</sup> and redox properties.<sup>29–31</sup> HATs have also been used to modify and control the color of mesoporous silica<sup>32</sup> and have been included in organic light emitting devices (OLEDs).<sup>33,34</sup>

Nonlinear optical (NLO) properties of HAT derivatives have been treated only once in the literature and only refer to some completely symmetric (trigonal) derivatives and its metal complexes with Cu<sup>+</sup>.<sup>35</sup> These molecules showed an octupolar NLO response.

Most of the HAT derivatives in the previous references involve trigonal molecules and only a few papers describe

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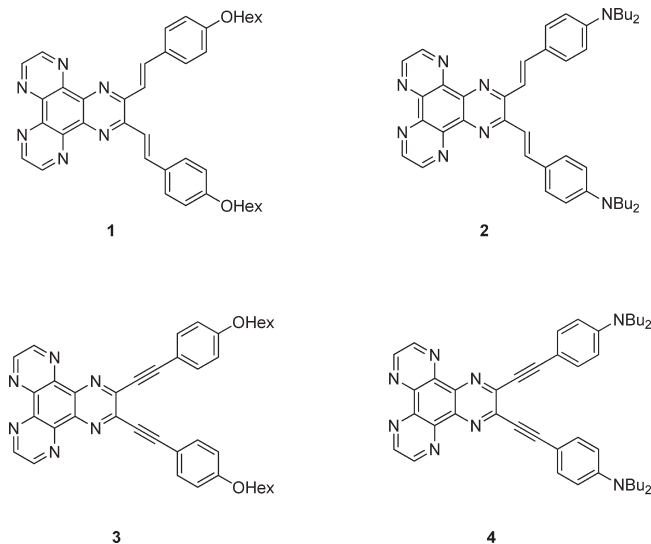
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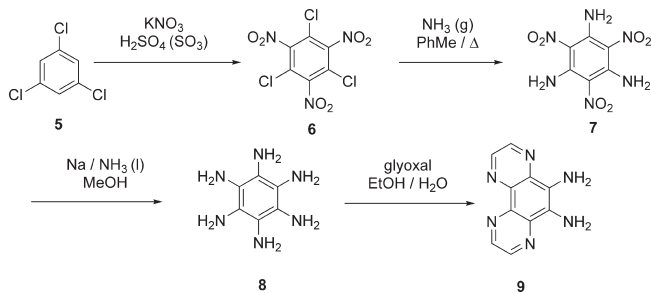
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## CHART 1. HATs Studied in the Present Paper



non-trigonal HAT derivatives.<sup>36–38</sup> All the properties of known HATs and the existence of very few synthetic routes to derivatives of nontrigonal HATs led us to propose new synthetic routes for molecules **1–4** (Chart 1). The aim of the present work is to provide full synthetic details to complete the previous preliminary communication<sup>39</sup> and describe new products to offer a wider scope of the properties of donor–acceptor nontrigonal HATs including their dipolar nonlinear optical properties.

## SCHEME 1. Synthesis of Hexaaminobenzene (**8**) and Diamine **9**



## 2. Results and Discussion

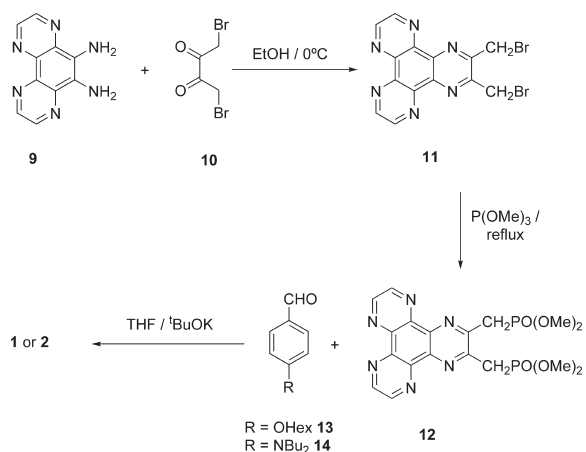
**2.1. Synthesis.** In the present work we present an experimental and theoretical study of V-shaped donor–acceptor HATs **1–4** (Chart 1) focusing on the NLO properties of the compounds. The molecules contain an HAT electron-deficient nucleus and two electron-donor peripheral substituents joined by an alkenyl (**1**, **2**) or alkynyl moiety (**3**, **4**). This design was adopted in order to generate a dipolar moment beneficial for a NLO response. In the preliminary communication we reported the synthesis of V-shaped HAT derivatives **1** and **2** starting from **9** (Scheme 1).<sup>39</sup> Diamine **9** could be obtained starting with the nitration of **5**,<sup>40</sup> substitution of chlorine atoms with ammonia to form **7**,<sup>41</sup> reduction of the nitro groups to yield hexaaminobenzene (**8**),<sup>42</sup> and finally condensation of **8** with two molecules of glyoxal.<sup>43</sup>

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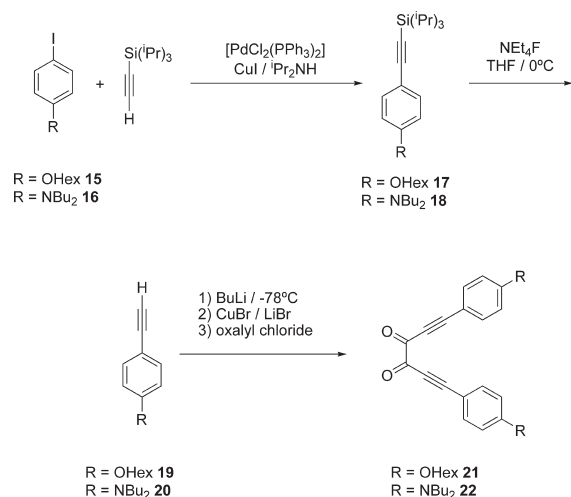
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**SCHEME 2. Synthesis of Key Products 11 and 12 and Final Obtention of Alkenyl-Linked Compounds 1 and 2**



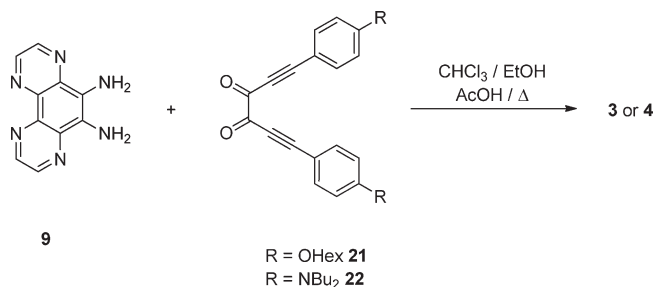
**SCHEME 3. Synthesis of Alkynyl  $\alpha$ -Diketones 21 and 22**



Diamine **9** can be condensed with 1,4-dibromobutadione (**10**) to obtain the HAT derivative **11** (Scheme 2). **11** is transformed into the diphosphonate **12** by heating in the presence of trimethylphosphite. Finally a Wittig–Horner reaction with the corresponding aldehyde (**13** or **14**) leads to the desired products **1** and **2** with yields of 60% and 25%, respectively. NMR spectra of the compounds show the *all-trans* configuration of the double bonds. Alkenyl protons appear like two doublets with a coupling constant of 15.2 Hz for compound **1** and 15.5 Hz for compound **2**. HAT moiety protons appear as two doublets at >9 ppm with a small coupling constant of 2.0 Hz. The rest of the signals can be assigned to the hexyloxybenzene or dibutylaminobenzene periphery.

For the synthesis of alkynyl-linked HATs **3** and **4** we have developed a different synthetic route that requires the preparation of diketones **21** and **22** (Scheme 3). The route starts with a Sonogashira cross-coupling reaction between **15** or **16** and triisopropylsilyl acetylene followed by deprotection in the presence of fluoride salts.

**SCHEME 4. Final Obtention of Alkynyl-Linked HATs 3 and 4**



**TABLE 1. Electrochemical Behavior of 1–4<sup>a</sup>**

compd	technique	$E_{\text{red}}^1$	$E_{\text{red}}^2$	$E_{\text{red}}^3$	$E_{\text{ox}}^1$	$E_{\text{ox}}^2$
1	CV	-1.38	-1.94		0.93	
	DPV	-1.36	-1.87	-2.39	0.96	1.26
2	CV	-1.39	-1.81		0.57	
	DPV	-1.39	-1.90		0.59	0.78
3	CV	-1.27			1.52	
	DPV	-1.20	-1.81		1.93	
4	CV	-1.29			0.81	
	DPV	-1.27	-1.85		0.86	1.03

<sup>a</sup>All measurements were obtained in dichloromethane solutions. Conditions: concentrations of 2 mM of sample and 0.1 M of HFPTBA. Pt working and auxiliary electrodes. Ag/Ag<sup>+</sup> reference electrode. Scan rate 100 mV/s. Values referenced to Fc/Fc<sup>+</sup>. All values are given in volts (V). In CV experiments  $E_{\text{red}}$  refers to  $E_{1/2}$  (half-wave potential) and  $E_{\text{ox}}$  to the onset of the process. In DPV all the values refer to the maximum of each redox signal.

The free terminal alkynes **19** and **20** have been previously reported starting from trimethylsilylacetylene precursors.<sup>44,45</sup> However, we preferred to use triisopropylsilyl as a protecting group due to its higher stability allowing us to store **17** and **18** for a long time without degradation when necessary. Alkynes **19** and **20** were then treated first with butyllithium, CuBr, and LiBr to effect the in situ formation of a dialkylcuprate intermediate that is immediately treated with oxalyl chloride to yield the  $\alpha$ -diketones **21** and **22**. Finally, condensation of diamine **9** and the corresponding diketone afforded the alkynyl-linked HATs **3** (63%) and **4** (36%) (Scheme 4).

NMR spectra show the HAT protons as a not solved multiplet at >9.2 ppm. The rest of the signals at high field correspond to the hexyloxy or dibutylaminobenzene terminal moieties. Alkyne groups appear clearly in the IR spectra. Both molecules show an intense and sharp signal at 2206 and 2186 cm<sup>-1</sup> for **3** and **4**, respectively, corresponding to the stretch of the triple bond.

**2.2. Electrochemistry.** The electrochemical behavior of the molecules was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dichloromethane. All molecules showed a donor–acceptor character with quasireversible reduction waves and irreversible oxidation processes (Table 1).

Alkynyl-linked HATs **3** and **4** showed better acceptor properties than alkenyl-linked HATs **1** and **2**.

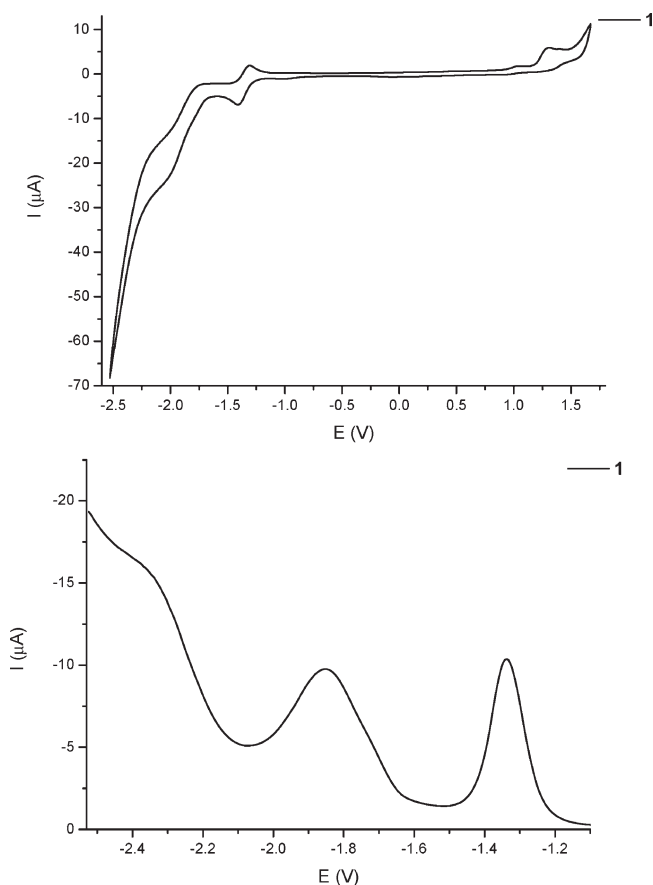
The oxidation potentials obtained by CV showed that the molecules with the hexyloxyphenyl groups were weaker electron donors (onset of 0.93 and 1.52 V for **1** and **3**, respectively) than the dibutylaminobenzene-substituted ones (onset of 0.57 and 0.81 V for **2** and **4**, respectively). In the cathodic regime,

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**FIGURE 1.** Electrochemistry of molecule **1**. Top: Cyclic voltammetry showing two quasireversible reduction waves. Bottom: Differential pulse voltammetry showing three reduction signals. Measurement conditions: see Table 1.

alkynyl molecules **3** and **4** showed first reduction potentials of  $-1.27$  and  $-1.29$  V, respectively, around  $100$  mV less negative than alkenyl-linked **1** (Figure 1, top), and **2**, which showed first reduction potentials of  $-1.38$  and  $-1.39$  V, respectively.

In CV only two of the three reduction waves for the HAT moiety<sup>46</sup> could be detected for molecules **1** and **2** and only the first one was observed for **3** and **4**. DPV experiments allowed the detection of the third reduction process for **1** (Figure 1, bottom). Probably this process was very near or beyond the solvent window for molecules **2**, **3**, and **4**. DPV studies also showed that the oxidation process for HATs **1**, **2**, and **4** consists of at least two different processes. Only one oxidation signal was observed for compound **3**. In this case again more processes could be located outside the solvent window.

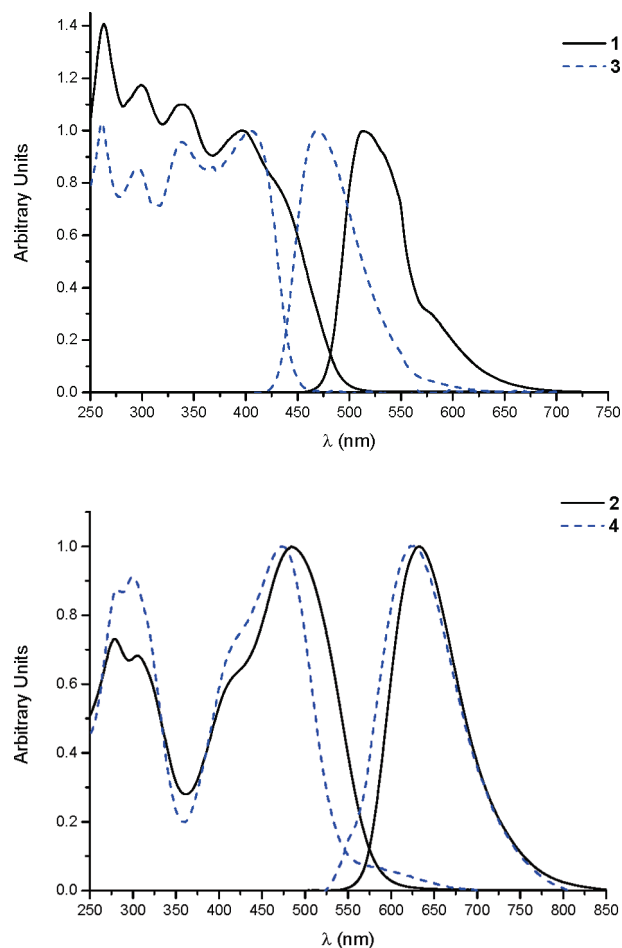
**2.3. Photophysical Studies.** Basic photophysical properties of the four molecules were investigated using absorption and emission spectroscopy. Absorption spectra showed that alkynyl-linked HATs **3** and **4** have larger extinction coefficients (Table 2) than alkenyl-linked HATs **1** and **2** although the shapes of the spectra are very similar (Figure 2).

If **1** and **3** are compared (Figure 2, top) it can be seen that the lowest energy absorption of **1** is red-shifted ( $420$  nm) compared with **3** ( $404$  nm). The same behavior can be seen for

**TABLE 2.** UV-vis Absorption and Emission Maxima<sup>a</sup>

compd	absorption		emission	
	$\lambda_{\max}$	$\epsilon$	$\lambda_{\text{exc}}$	$\lambda_{\text{em}}$
<b>1</b>	420	18 046	420	513
<b>2</b>	490	54 511	490	633
<b>3</b>	404	158 482	404	469
<b>4</b>	473	144 066	473	624

<sup>a</sup>All measurements were recorded in dichloromethane with a sample concentration of  $0.001$  mM. Wavelengths are given in nm and molar extinction coefficients in  $\text{M}^{-1} \text{cm}^{-1}$ .



**FIGURE 2.** Top: Absorption (left) and emission spectra (right) of molecules **1** (solid line: excitation wavelength  $420$  nm) and **3** (dashed line: excitation wavelength  $404$  nm). Bottom: Absorption and emission spectra of molecules **2** (solid line: excitation wavelength  $490$  nm) and **4** (dashed line: excitation wavelength  $473$  nm). Spectra were recorded in  $0.001$  mM solutions in dichloromethane.

dibutylaminobenzene-substituted HATs (Figure 2, bottom). The lowest energy transition of **2** is bathochromically shifted ( $490$  nm) compared with **4** ( $473$  nm). When the lowest energy transition is excited the fluorescence spectra can be collected. Again emission of alkenyl-linked HATs is red-shifted ( $513$  and  $633$  nm for **1** and **2**, respectively) compared to that of alkynyl-linked HATs ( $469$  and  $624$  nm for **3** and **4**, respectively). It can be observed that the **2** and **4** emission maxima differ only by  $9$  nm but the difference for the emission maxima of **1** and **3** is  $44$  nm (Figure 2, Table 2).

The nonlinear optical properties of compounds **1–4** were studied with the EFISH technique at  $1.907$  nm in

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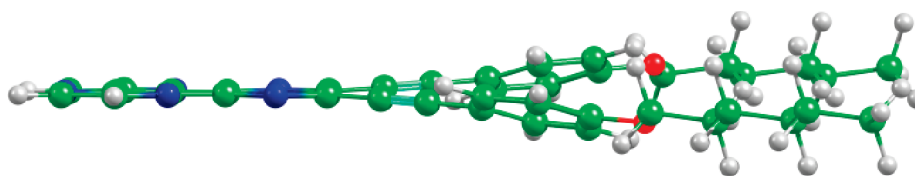


FIGURE 3. Side view of the B3P86/6-31G\* optimized  $C_2$  geometry (the optimization was constrained) of compound **3**.

TABLE 3. Results of Theoretical Calculations

compd	TD-DFT <sup>a</sup>						CPHF <sup>b</sup>		
	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	sym.	$E_{01}$	$\mu_{01}$	$\Delta\mu_{01}$	$\beta_{zzz}(0)$	$\beta_{zyy}(0)$	$\mu\beta(0)$
<b>1</b>	-5.81	-2.73	A	2.71	5.8	11.9	30	26	114
			B	2.87	7.3	10.3			
			B	3.18	4.6	10.3			
<b>2</b>	-5.31	-2.49	A	3.40	8.2	11.3	51	46	596
			A	2.48	5.8	9.6			
			B	2.59	7.2	12.7			
<b>3</b>	-6.12	-2.78	B	2.80	5.7	12.5	39	16	201
			A	3.02	8.5	14.4			
			A	2.97	5.5	12.0			
<b>4</b>	-5.55	-2.56	A	2.97	5.4	10.1	66	28	731
			B	3.35	2.4	12.0			
			A	3.34	8.3	11.3			
			B	2.64	5.6	15.4			
			A	2.68	4.9	13.9			
			B	2.94	3.4	16.5			
			A	3.04	9.8	17.1			

<sup>a</sup>B3P86/6-31G\*, energies are in eV, dipoles in Debye. <sup>b</sup>HF/6-31G\*, hyperpolarizabilities  $\beta$  in  $10^{-30}$  esu and  $\mu\beta$  in  $10^{-48}$  esu.

dichloromethane. Similar  $\mu\beta$  values, around  $1000 \times 10^{-48}$  esu, were obtained for dibutylamino derivatives **2** and **4** ( $1010(50) \times 10^{-48}$  and  $970(50) \times 10^{-48}$  esu, respectively). As expected from the relative donor strength of substituents, much lower response was observed for hexyloxy benzene derivatives.  $\mu\beta = 200(30) \times 10^{-48}$  esu was obtained for compound **3** whereas the nonlinear optical response of **1** was too small to be reliably determined. For the sake of comparison, Disperse Red 1, a common benchmark of organic NLO-Chromophores, gives a  $\mu\beta(0)$  value of ca.  $480 \times 10^{-48}$  esu in the same experimental conditions.

**2.4. Theoretical Calculations.** The molecular geometries of compounds **1–4** have been optimized constrained to  $C_2$  symmetry by using the hybrid B3P86 DFT (density functional theory) method and the 6-31G\* basis set. The  $\pi$  systems in ethylenic compounds **1** and **2** are completely planar, but this is not the case for acetylenic chromophores **3** and **4** (see Figure 3): The folding angle defined by one of the substituents, the HAT moiety, and the other substituent is  $3.6^\circ$ . Furthermore, the substituted phenyl rings are twisted by  $15^\circ$  (**3**) or  $13.4^\circ$  (**4**) with respect to the HAT moiety. On the basis of structural parameters, a better  $\pi$  delocalization is expected for ethylenic than for acetylenic compounds.

The properties of compounds **1–4** studied by theoretical methods are gathered in Table 3. While it is not possible to match precisely theoretical calculations performed on isolated molecules in the gas phase to experimental measurements performed in solution, the results of the calculations allow a qualitative description of the observed trends. It can be seen that the HOMO energy is higher for dialkylamino compounds than for their analogous alkoxy compounds by 0.50–0.57 eV thus explaining the less positive oxidation potential of the former. In a similar way the HOMO and LUMO energies of ethylenic compounds are higher

than that of their acetylenic analogues (compare **1** to **3** and **2** to **4**) in good agreement with the lower oxidation and more negative reduction potential of **1** compared to **3** and **2** compared to **4**.

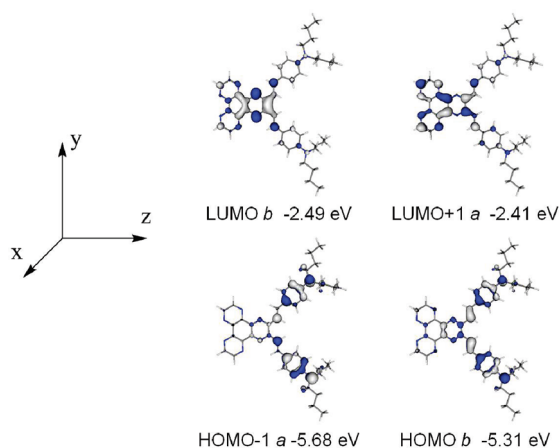
The absorption spectra calculated by TD-DFT (time-dependent density functional theory) predict the lowest excitation energies with an error of 0.24 eV for compound **1** and less than 0.1 eV for **2–4**, which is a reasonable error for this method. We have previously mentioned that replacement of a double by a triple bond decreases the energy of both the HOMO and the LUMO; according to our calculations this effect is more important on the HOMO and therefore causes an increased HOMO–LUMO gap that results in a hypsochromic shift. In a similar way, on passing from hexyloxy to dibutylamino substituent the HOMO energy increases by 0.50 eV (from **1** to **2**) or 0.57 eV (from **3** to **4**) while the LUMO energy increases by 0.24 and 0.22 eV, respectively, and therefore there is a decreased HOMO–LUMO gap and the absorption of dibutylamino derivatives is red-shifted with respect to their hexyloxy analogues.

Molecules **1–4** belong to the so-called V-shaped (or  $\Lambda$ -shaped) chromophores<sup>47</sup> displaying  $C_2$  symmetry. Making use of the standard orientation, we assume that the molecule lies on the  $yz$  plane with  $z$  along the symmetry axis (see Figure 4). The molecular hyperpolarizability is dominated by two tensor components:  $\beta_{zzz}$  and  $\beta_{zyy}$  (the off-diagonal component) and the EFISH technique samples  $\mu\beta$  values contributed from both tensor components:

$$\mu\beta = \mu\beta_z = \mu(\beta_{zzz} + \beta_{zyy})$$

A simple model to study the NLO properties describes  $C_2$  chromophores as the combination of two isolated

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**FIGURE 4.** A 0.04 contour plot of the molecular orbitals of **2** involved in the four lowest energy electronic transitions.

chromophores in one molecule.<sup>48</sup> Using this approach, the above-mentioned tensor components can be calculated as:

$$\beta_{zzz} = 2 \cos^3(\alpha/2)\beta_1$$

$$\beta_{zyy} = 2 \cos(\alpha/2) \sin^2(\alpha/2)\beta_1$$

where  $\beta_1$  is the hyperpolarizability of a single chromophore and  $\alpha$  is the angle formed by the two chromophores in the molecule. It can be concluded that the ratio of the two tensor components depends on the angle formed by the two chromophores ( $\beta_{zyy}/\beta_{zzz} = \tan^2(\alpha/2)$ ) and therefore the two-dimensional character of a given molecule increases with the angle formed by the two chromophores. The angle described by the heteroatom substituting the phenyl ring (O in **1** and **3**, N in **2** and **4**), the center of the HAT moiety, and the heteroatom substituting the other phenyl ring is 71° in ethylenic compounds **1** and **2** and 49° in derivatives **3** and **4**. Therefore, on only the basis of the molecular geometries, it is expected that  $\beta_{zyy}$  should be smaller than  $\beta_{zzz}$  for all the studied compounds and that ethylenic compounds should have a larger two-dimensional character than their acetylenic analogues.

To get further insight into the nonlinear optical properties of these compounds the zero frequency molecular hyperpolarizability was calculated as the analytical second derivative of the dipole moment with respect to the electric field using the Coupled Perturbed Hartree–Fock (CPHF) method. Experimental  $\mu\beta$  values cannot be easily extrapolated to zero frequency due to the two-dimensional character of these chromophores that gives rise to several excited states close in energy. However, a reasonable agreement between theoretical and experimental data can be found if we assume that compound **2** having lower excitation energies than **4** displays a larger resonance enhancement when measuring the NLO properties at 1.9 nm and therefore while the  $\mu\beta(0)$  value is somewhat larger for **4**, the  $\mu\beta$  values measured for these compounds are similar.

As expected from molecular geometries, the CPHF-calculated  $\beta_{zzz}$  is always larger than  $\beta_{zyy}$  and a larger off-diagonal

component is found for ethylenic compounds compared to their acetylenic analogues.

A commonly used<sup>48–52</sup> intuitive explanation to the origin of the nonlinear optical response in V-shaped chromophores assumes that it mainly arises from transitions from the ground to excited states (in other words that the contribution of transitions between excited states to the hyperpolarizability is negligible). Making use of a “simplified multistate two-level treatment”, the contribution of each excited state to the hyperpolarizability can be calculated as:

$$\beta_{0e} \rightarrow \mu_{0e}^2 \Delta\mu_{0e} / \Delta E_{0e}^2$$

where  $\mu_{0e}$  is the transition dipole,  $\Delta\mu_{0e}$  the dipole moment difference between ground and excited state, and  $\Delta E_{0e}$  the excitation energy.

Figure 4 shows the molecular orbitals involved in the lowest energy transitions of compound **2**. Transitions between orbitals with the same symmetry (HOMO  $\rightarrow$  LUMO and HOMO-1  $\rightarrow$  LUMO+1) have *A* symmetry, are therefore polarized along the *z* axis, and contribute to  $\beta_{zzz}$ . On the other hand, transitions between orbitals with different symmetry (HOMO  $\rightarrow$  LUMO+1 and HOMO-1  $\rightarrow$  LUMO) have *B* symmetry, are polarized along the *y* axis, and contribute to  $\beta_{zyy}$ . The calculated parameters contributing to this multiple two-state approach are gathered in Table 3. It can be seen that, for each electronic transition, there is a close-in-energy transition with a different symmetry but similar  $\mu_{0e}$  and  $\Delta\mu_{0e}$ . This fact explains the analogous values obtained for the two tensor components ( $\beta_{zzz}$  and  $\beta_{zyy}$ ) in each of the studied compounds. The enhanced NLO response of amino derivatives **2** and **4** compared to **1** and **3** can be explained on the basis of the lower  $\Delta E_{0e}$  calculated for dibutylamino derivatives that is experimentally confirmed by their absorption spectra.

### 3. Conclusions

In conclusion, we have developed a new series of hexaazatriphenylene derivatives as novel V-shaped chromophores displaying  $C_2$  symmetry suitable for nonlinear optical investigations. By varying the type of linker and the nature of the donor moiety, the electrochemical properties as well as the absorption spectra of the well-defined asymmetric donor–acceptor conjugated systems can facilely be tuned. By using the EFISH technique high  $\mu\beta$  values have been obtained for the systems containing the more electron-rich dibutylamino moiety. To get further insight on the nonlinear optical properties of these compounds we have performed theoretical calculations and found that there is a reasonable qualitative agreement between experimental and calculated hyperpolarizabilities. Additionally, the theoretical calculations support the two-dimensional NLO character of these chromophores. The versatility of the synthetic routes described above paves the way for the functionalization of the

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HAT moiety with different moieties to further tune their nonlinear optical response.

#### 4. Experimental Section

**2,3-Bis(bromomethyl)hexaazatriphenylene (11).** To a stirred suspension of diamine (**9**) (673 mg, 3.17 mmol) in absolute ethanol (70 mL) at 0 °C under argon atmosphere was added 1,4-dibromobutanedione (**10**) (1.161 g, 4.76 mmol). The suspension was stirred for 5 h at that temperature, then the solvent was removed under vacuum. The crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> until unchanged butanedione was eluted then CH<sub>2</sub>Cl<sub>2</sub> with 2% MeOH). A pale-yellow solid were isolated (1.265 g, 95%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ (ppm) 9.33 (d, 2H, *J* = 2.0 Hz), 2.29 (d, 2H, *J* = 2.0 Hz), 5.18 (s, 4H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ (ppm) 154.1, 147.2, 147.1, 142.5, 141.7, 140.8, 29.6. FTIR (KBr) ν (cm<sup>-1</sup>) 3030, 2970, 2923, 1631, 1380, 1092. MS (EI) *m/z* (%) 418 [M]<sup>+</sup> (3), 262 (100), 221 (64). Elemental Anal. Calcd: C (40.03), H (1.92), N (20.01). Found: C (40.19), H (2.05), N (19.87). Mp > 170 °C dec.

**2,3-Bis((dimethylphosphonate)methyl)hexaazatriphenylene (12).** A suspension of **11** (161 mg, 0.38 mmol) in trimethylphosphite (15 mL) under Argon atmosphere was heated to reflux for 3 h. After this time an excess of solvent was distilled and the residue was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>: MeOH 9:1). The product was obtained as a pale-brown solid (102 mg, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.28 (d, 2H, *J* = 2.0 Hz), 9.25 (d, 2H, *J* = 2.0 Hz), 4.30 (d, 4H, *J* = 22.0 Hz), 3.80 (d, 12H, *J* = 11.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 151.5, 146.9, 146.6, 142.2, 142.0, 140.1, 53.2, 34.2 (d, CH<sub>2</sub>-P, *J* = 132.0). FTIR (KBr) ν (cm<sup>-1</sup>) 2958, 1635, 1542, 1239, 1030. MS (EI) *m/z* (%) 478 [M]<sup>+</sup> (100), 384 (30), 275 (33), 94 (36). Elemental Anal. Calcd: C (45.20), H (4.21), N (17.57). Found: C (45.02), H (3.98), N (17.65). Mp > 220 °C dec.

**4-Hexyloxybenzaldehyde (13).** In a round-bottomed flask *p*-hydroxybenzaldehyde (2 g, 16 mmol), hexyl bromide (3.46 g, 21 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.94 g, 21 mmol) were dissolved in DMF (50 mL). The solution was heated to reflux for 16 h and then allowed to cool to room temperature. The reaction was poured into water and extracted with dichloromethane. The organic phase was dried over MgSO<sub>4</sub> and filtered and the solvent was removed in vacuo. The oil obtained was purified by column chromatography (silica gel), using a mixture of hexane:ethyl acetate (7: 3) as eluent, to yield 2.877 g of product as a pale yellow oil (87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.87 (s, 1H), 7.82 (d, 2H, *J* = 8.4 Hz), 6.99 (d, 2H, *J* = 8.4 Hz), 4.04 (t, 2H, *J* = 6.5 Hz), 1.81 (m, 2H), 1.47 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 190.8, 164.2, 131.9, 129.7, 114.7, 68.4, 31.5, 29.0, 25.6, 22.6, 14.0. FTIR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>) 2931, 2863, 2733, 1691, 1601, 1509, 1310, 1256, 1159, 1015, 832. MS (ESI) *m/z* 229.0 [M + Na]<sup>+</sup>. Elemental Anal. Calcd: C (75.69), H (8.80). Found: C (75.75), H (8.63).

**General Procedure for the Synthesis of 1 and 2.** A suspension of phosphonate (**12**) (80 mg, 0.17 mmol) and the corresponding aldehyde (**13** or **14**) (0.37 mmol) in dry THF (10 mL) under argon atmosphere was heated to reflux, then potassium *tert*-butoxide (56 mg, 0.50 mmol) was added. The solution was refluxed for 3 h and then allowed to cool to room temperature and methanol (5 mL) was added. After the solvent was removed the residue was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> until elution of unchanged aldehyde and then CH<sub>2</sub>Cl<sub>2</sub> with 2% MeOH).

**HAT-Alkene(OHex)<sub>2</sub> (1):** A yellow-orange solid was isolated (64 mg, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.22 (d, 2H, *J* = 2.1 Hz), 9.21 (d, 2H, *J* = 2.1 Hz), 8.23 (d, 2H, *J* = 15.2 Hz), 7.67 (d, 4H, *J* = 9.0 Hz), 7.59 (d, 2H, *J* = 15.2 Hz), 6.95 (d, 4H, *J* = 9.0 Hz), 4.01 (t, 4H, *J* = 7.3 Hz), 1.90–1.70 (m, 4H), 1.57–1.2 (m, 12H), 0.92 (t, 6H, *J* = 7.0 Hz). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>) δ (ppm) 160.4, 150.9, 146.7, 154.8, 142.6, 141.9, 139.7, 139.3, 129.4, 128.9, 119.5, 114.8, 68.1, 31.6, 29.2, 25.7, 22.6, 14.0. FTIR (KBr) ν (cm<sup>-1</sup>) 2929, 2858, 1602, 1509, 1249, 1172, 754. MS (EI) *m/z* (%) 638 [M]<sup>+</sup> (100), 553 (25). Elemental Anal. Calcd: C (75.21), H (6.63), N (13.16). Found: C (75.32), H (6.58), N (13.18). Mp 237–239 °C.

**HAT-Alkene(NBu)<sub>2</sub> (2):** A red solid was obtained (29 mg, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.25 (d, 2H, *J* = 2.2 Hz), 9.17 (d, 2H, *J* = 2.2 Hz), 8.24 (d, 2H, *J* = 15.5 Hz), 7.63 (d, 4H, *J* = 9.0 Hz), 7.53 (d, 2H, *J* = 15.5 Hz), 6.67 (d, 4H, *J* = 9.0 Hz), 3.34 (t, 8H, *J* = 8.3 Hz), 1.70–1.52 (m, 8H), 1.49–1.22 (m, 8H), 0.98 (t, 12H, *J* = 7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 151.6, 149.1, 146.6, 145.4, 142.9, 141.7, 140.2, 138.8, 133.3, 129.7, 123.6, 116.5, 111.4, 50.8, 29.5, 20.3, 13.9. FTIR (KBr) ν (cm<sup>-1</sup>) 2958, 2931, 1598, 1522, 1502, 1368, 1183. MS (EI) *m/z* (%) 692 [M]<sup>+</sup> (21), 640 (88), 368 (62), 449 (91), 107 (100). Elemental Anal. Calcd: C (76.27), H (7.56), N (16.17). Found: C (76.18), H (7.63), N (16.23). Mp 184 °C.

**General Procedure for the Synthesis of 17 and 18.** To a solution under argon atmosphere of the corresponding iododerivative (**15** or **16**) (6.58 mmol) and triisopropylsilylacetylene (6.58 mmol) in diisopropylamine (20 mL) were added [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (230 mg, 0.33 mmol) and CuI (106 mg, 0.56 mmol). The suspension was stirred at room temperature for 16 h. After this time 50 mL of hexane was added and the reaction was filtered over a plug of silica with dichloromethane as eluent. The solvent was then removed and the residue purified by column chromatography (silica gel, hexane).

**((4-(Hexyloxy)phenyl)ethynyl)triisopropylsilane (17):** The product was obtained as a colorless oil (1.975 g, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.40 (d, 2H, *J* = 9.1 Hz), 6.80 (d, 2H, *J* = 9.1 Hz), 3.94 (t, 2H, *J* = 6.6 Hz), 1.77 (quint, 2H, *J* = 6.6 Hz), 1.45 (m, 2H), 1.33 (m, 4H), 1.12 (s, 18H), 1.09 (s, 3H), 0.9 (t, 3H, *J* = 7.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 159.1, 133.4, 115.4, 114.2, 107.16, 88.4, 68.0, 31.5, 29.1, 25.6, 18.7, 14.0, 11.3. FTIR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>) 2938, 2864, 2153, 1605, 1506, 1246, 882, 831, 782. MS (ESI) *m/z* 381.3 [M + Na]<sup>+</sup>. Elemental Anal. Calcd: C (77.03), H (10.68). Found: C (76.99), H (10.75).

***N,N*-Dibutyl-4-((triisopropylsilyl)ethynyl)aniline (18):** The product was obtained as a light yellow oil (2.32 g, quantitative). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.31 (d, 2H, *J* = 9.0 Hz), 6.52 (d, 2H, *J* = 9.0 Hz), 3.26 (t, 4H, *J* = 7.6 Hz), 1.54 (quint, 4H, *J* = 7.6 Hz), 1.33 (sext, 4H, *J* = 7.7 Hz), 1.16–1.06 (m, 21H), 0.94 (t, 6H, *J* = 7.3 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 147.9, 133.3, 111.1, 109.3, 108.7, 86.8, 50.7, 29.4, 20.3, 18.7, 13.9, 11.5. FTIR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>) 2939, 2863, 2144, 1605, 1514, 1461, 1366, 1184. MS (ESI) *m/z* 408.3 [M + Na]<sup>+</sup>. Elemental Anal. Calcd: C (77.85), H (11.24), N (3.63). Found: C (78.02), H (11.11), N (3.51).

**General Procedure for the Synthesis of 21 and 22<sup>53</sup>.** Under argon atmosphere the corresponding unprotected alkyne (**19** or **20**) (3.96 mmol) was dissolved in anhydrous THF (15 mL) at 0 °C. To this solution was added butyllithium (3.96 mmol, 1.6 M in hexanes) slowly and the resulting solution was stirred for 30 min. Meanwhile a second solution was prepared dissolving LiBr (688 mg, 7.92 mmol) and CuBr (568 mg, 3.96 mmol) under argon atmosphere in anhydrous THF (50 mL) at 0 °C. The first solution was slowly added to the second and then the resulting mixture was stirred. After 10 min oxalyl chloride (226 mg, 1.78 mmol) was added slowly. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature. The solution was then poured into a saturated solution of NH<sub>4</sub>Cl. The organic phase was separated and the aqueous phase extracted with two portions of ether. The organic extracts were dried with MgSO<sub>4</sub> and filtered and the solvent was removed.

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**1,6-Bis(4-(hexyloxy)phenyl)hexa-1,5-diyne-3,4-dione (21):**

The solid obtained was purified by column chromatography (silica gel), using a mixture of hexane:dichloromethane (6.5:3.5). The product was isolated as a yellow solid (53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.64 (d, 4H, *J* = 8.8 Hz), 6.91 (d, 4H, *J* = 8.8 Hz), 4.00 (t, 4H, *J* = 6.5 Hz), 1.79 (q, 4H, *J* = 6.7 Hz), 1.46 (m, 4H), 1.38–1.29 (m, 8H), 0.90 (t, 6H, *J* = 5.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 172.7, 162.2, 136.2, 115.0, 110.6, 101.8, 86.9, 68.3, 31.5, 29.0, 25.6, 22.6, 14.0. FTIR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>) 2933, 2863, 2187, 1661, 1600, 1509, 1255, 1174, 999, 835. MS (ESI) *m/z* 481.3 [M + Na]<sup>+</sup>. Elemental Anal. Calcd: C (78.57), H (7.47). Found: C (78.39), H (7.55). Mp 103–105 °C

**1,6-Bis(4-(dibutylamino)phenyl)hexa-1,5-diyne-3,4-dione (22):**

The solid obtained was purified by column chromatography (Et<sub>3</sub>N deactivated silica gel, light exclusion) with a mixture of hexane:dichloromethane (5:5). The product was isolated as a red solid (16%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.54 (d, 4H, *J* = 9.1 Hz), 6.58 (d, 4H, *J* = 9.1 Hz), 3.32 (t, 8H, *J* = 7.6 Hz), 1.59 (quint, 8H, *J* = 7.7 Hz), 1.36 (sext, 8H, *J* = 7.6 Hz), 0.97 (t, 12H, *J* = 7.3 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 173.0, 150.6, 136.4, 111.3, 105.4, 103.9, 89.5, 50.7, 29.3, 20.2, 13.9. FTIR (CH<sub>2</sub>Cl<sub>2</sub>) ν (cm<sup>-1</sup>) 2957, 2867, 2159, 1645, 1589, 1522, 1365, 1189, 983. MS (MALDI/TOF) *m/z* 513.2 [M + H]<sup>+</sup>. Elemental Anal. Calcd: C (79.65), H (8.65), N (5.46). Found: C (79.48), H (8.64), N (5.59). Mp 104–106 °C

**General Procedure for the Synthesis of 3 and 4.** A solution of diamine (**9**) (0.47 mmol) and the corresponding diketone (**21** or **22**) (0.56 mmol) in chloroform (10 mL), ethanol (10 mL), and acetic acid (1 mL) was heated to reflux for 2 h. After this time the solution was allowed to cool to room temperature. The reaction was treated with a saturated solution of NaHCO<sub>3</sub> and brine. The organic phase was dried over MgSO<sub>4</sub> and filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) with dichloromethane (2% methanol) as solvent.

**HAT-Alkyne(OHex)<sub>2</sub> (3):** The product was isolated as a yellow solid (63%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.18 (m, 4H), 7.57 (d, 4H, *J* = 8.3 Hz), 6.84 (d, 4H, *J* = 8.3 Hz), 3.93 (t, 4H, *J* = 6.5 Hz), 1.73 (m, 4H), 1.39 (m, 4H), 1.28 (m, 8H), 0.84 (t, 6H, *J* = 6.7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 160.6, 146.5, 143.5, 141.7, 138.9, 134.1, 128.2, 114.7, 113.1, 99.7, 86.5, 68.1, 31.4, 29.0, 25.6, 22.5, 13.9. FTIR (KBr) ν (cm<sup>-1</sup>) 3047, 2929, 2862, 2206, 1602, 1511, 1244, 1126, 831. MS (MALDI/TOF) *m/z* 635.2 [M + H]<sup>+</sup>. Elemental Anal. Calcd: C (75.69), H (6.03), N (13.24). Found: C (75.83), H (5.85), N (13.25). Mp 210 °C.

**HAT-Alkyne(NBu)<sub>2</sub> (4):** The product was isolated as a red solid (36%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.22 (m, 4H), 7.56 (d, 4H, *J* = 8.3 Hz), 6.59 (d, 4H, *J* = 8.3 Hz), 3.30 (t, 8H, *J* = 7.5 Hz), 1.59 (m, 8H), 1.37 (m, 8H), 0.96 (t, 12H, *J* = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 149.1, 146.8, 146.1, 143.8, 141.8, 138.3, 134.3, 111.0, 106.6, 102.4, 87.2, 50.6, 29.2, 20.2, 13.9. FTIR (KBr) ν (cm<sup>-1</sup>) 2956, 2927, 2865, 2186, 1603, 1523, 1368, 1182, 812. MS (MALDI/TOF) *m/z* 689.3 [M + H]<sup>+</sup>. Elemental Anal. Calcd: C (76.71), H (7.02), N (16.27). Found: C (76.82), H (7.09), N (16.42). Mp 240–242 °C.

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**Supporting Information Available:** Experimental and theoretical details and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.