

Like cyanines, yet different: New cationic dyes, which have alkyne bridges between the indole end groups, have been synthesized. Despite the large bond-length alternation (BLA), these carbocations display cyanine-like non-

linear optical behavior, such as large negative third-order hyperpolarizabilities, although exhibiting two-photon absorption behavior similar to that of triarylmethyl carbocations, such as brilliant green (see figure).

Cyanine-Like Dyes with Large Bond-**Length Alternation** 



# **Cyanine-Like Dyes with Large Bond-Length Alternation**

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**Abstract:** Herein, the synthesis and properties of alkyne-bridged carbocations, which are analogous in structure to cyanine dyes, are reported. An alkene-bridged dye, linked at the third position of the indole, was also synthesized as a reference compound. These new carbocations are stable under ambient conditions, allowing characterization by UV/Vis and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopies. These techniques revealed a large degree of delocalization of the positive charge, similar to a pre-

viously reported porphyrin carbocation. The linear and nonlinear optical properties are compared with cyanine dyes and triarylmethyl cations, to investigate the effects of the bond-length alternation and the overall molecular geometry. The value of  $\text{Re}(\gamma)$ , the real part of the third-order microscopic polarizability, of  $-1.3 \times 10^{-33}$  esu for the

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alkyne-linked cation is comparable to that of a cyanine dye of similar length. Nondegenerate two-photon absorption spectra showed that the alkene-bridged dye exhibited characteristics of cyanines, whereas the alkyne-bridged dye is reminiscent of octupolar chromophores, such as the triarylmethyl carbocation brilliant green. Such attributes were confirmed and rationalized by quantum chemical calculations.

# Introduction

Cyanine dyes have been studied extensively due to their exceptional linear and nonlinear optical (NLO) properties, leading to applications in biological imaging,<sup>[1]</sup> optical-data storage,<sup>[2]</sup> and all-optical switching.<sup>[3]</sup> For example, extended cyanine dyes tend to have a large negative real part of the third-order polarizability,  $Re(\gamma)$ , in the telecommunication wavelength range ( $\lambda = 1.3-1.6 \,\mu m$ ), making them relevant for all-optical switching applications, although having low values of the imaginary third-order polarizability,  $Im(\gamma)$ , thus minimizing optical losses by two-photon absorption (2PA).<sup>[3]</sup> The strong electronic delocalization and intense low energy absorption bands of cyanine dyes are associated with a lack (or very limited extent) of bond-length alternation.<sup>[4]</sup> Recently, in a computational study, we identified model alkyne carbocations with large bond-length alternation, which exhibited cyanine-like properties (Figure 1).<sup>[5]</sup>

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Figure 1. Cyanine and alkyne-cyanine structures.

Subsequently, Jacquemin compared the polarizabilities of the "alkynes–cyanines" to those of conventional cyanines, at the DFT level.<sup>[6]</sup> However, experimental characterization of the NLO properties of the "alkyne–cyanines" had not been carried out to date, due to the lack of suitably stable alkyne carbocationic systems.

Alkyne-bridged carbocations similar to the structure shown in Figure 1 have been reported by Nakatsuji et al.<sup>[7]</sup> Extension of one arm of a triarylmethyl carbocation with an ethynyl group resulted in a redshift of the absorption spectrum. Extension of more than one arm caused a large decrease in stability and gave a pyrylium cation decomposition product. Komatsu et al. successfully measured linear absorption and NMR spectra of similar dyes,<sup>[8]</sup> but such experiments were only possible at low temperature or over time periods of seconds. Arisandy et al. reported the synthesis of ferrocenyl cations with two cyclopentadiene units linked by either an alkene or alkyne bridge;<sup>[9]</sup> although the alkenelinked cations were very stable, the alkyne-linked cations rapidly decomposed to give unidentifiable products. A ruthenium-stabilized ethynyl cation, which was stable under anaerobic conditions, has also been reported.[10]

Herein, we present the synthesis of alkyne-bridged cyanine analogues and explore the effect of the inherent bondlength alternation and chemical structure on the molecular

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properties. The resulting dyes are stable for long periods of time under ambient conditions, which allowed us to investigate their properties by using a wide range of techniques. <sup>13</sup>C NMR analysis of isotopically enriched cations provided insight into the degree of charge delocalization. The linear and nonlinear optical properties were compared with an alkene-linked carbocation, as well as commercially available cyanines and triarylmethyl carbocations, by using femtosecond-pulsed *Z*-scan and nondegenerate 2PA techniques.

## **Results and Discussion**

Our first approach to synthesizing alkyne–cyanines followed the route shown in Scheme 1 (compounds  $1a-7a^+$ ; R=H). Regioselective 3-iodination of indole 1a was carried out as



Scheme 1. Synthesis of alkyne–cyanines  $7a^+$  and  $7b^+$ . a) I<sub>2</sub>, KOH, DMF; 2a 55%; b) MeI, NaH, DMF; 3a 88%, 3b 98%; c) for 4a: HCCSiMe<sub>3</sub>, [Pd<sub>2</sub>(dba)<sub>3</sub>], PPh<sub>3</sub>, CuI, PhMe, NEt<sub>3</sub>, 40°C, 40%; for 4b: 2-methyl-3butyn-2-ol, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, DMF, NEt<sub>3</sub>, 61%; d) for 5a: Bu<sub>4</sub>NF, CH<sub>2</sub>Cl<sub>2</sub>, 99%; for 5b: NaOH, PhMe, 100°C, 50%; e) LiN(SiMe<sub>3</sub>)<sub>2</sub>, PhCO<sub>2</sub>Me, THF; 6a 78%, 6b 95%; f) CF<sub>3</sub>CO<sub>2</sub>H, CHCl<sub>3</sub>, or HBF<sub>4</sub>·Et<sub>2</sub>O, Et<sub>2</sub>O, 87% (7b<sup>+</sup>).

was reported by Bocchi and Palla.<sup>[11]</sup> *N*-Methylation proved essential to the stability of the iodinated indole. Sonogashira coupling under standard conditions gave the alkynyl indole **4a**. Alcohol **6a** was synthesized directly from the deprotected ethynyl indole and methyl benzoate. The presence of a base (NEt<sub>3</sub>) in the chromatography eluent was necessary to avoid decomposition of these alkynes on silica.

Alkyne–cyanine  $7a^+$  was formed by addition of trifluoroacetic acid (2%; v/v) to a solution of alcohol **6a** in chloroform. Initially, the absorption showed an intense cyaninelike band at  $\lambda = 750$  nm (Figure 2). This absorption band became less intense over time, and there was a concomitant shift in the absorption band to around  $\lambda = 550$  nm. By monitoring the intensity of the  $\lambda = 750$  nm absorption band over time, the rate of decomposition was found to depend on the acid concentration.<sup>[12]</sup>



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Figure 2. Normalized absorption spectra of alkynyl cations  $7a^+$  (solid line) and  $7b^+$  (dashed line) recorded in CHCl<sub>3</sub>/2 % TFA at 298 K.

To facilitate photophysical studies, it was necessary to synthesize a more stable version of the alkyne-cyanine. This was achieved by incorporation of a 2-phenyl substituent on the indole (Scheme 1, compounds  $1b-7b^+$ ; R = Ph). The additional phenyl groups stabilize the cationic species, probably by hindering nucleophilic attack. The silyl-protected 2-phenyl indole could not be separated from iodoindole 3b and from Sonogashira coupling by-products due to the high mobility of these compounds on silica; therefore, an alcohol-protecting group was used (4b). The disadvantage of the new protecting group was the lower yield in the deprotection step. The alkyne-cyanine was generated in solution by addition of trifluoroacetic acid (TFA; 2%) to a solution of **6b** in CHCl<sub>3</sub>. The near-IR absorption band of  $7b^+$  is redshifted by approximately 50 nm from that of  $7a^+$ . By monitoring the absorption over time, it was seen that the 2-Ph alkyne-cyanine is substantially more stable than the 2-H alkyne-cyanine.<sup>[12]</sup> The cation was still observed by <sup>1</sup>H NMR and absorption spectroscopy after one week in solution in CHCl<sub>3</sub>/2% TFA at about 50% of the original concentration.

As well as forming the stable carbocation  $7b^+$  in solution for absorption and NMR experiments, the tetrafluoroborate salt was isolated as a solid in a high yield (87%). Addition of tetrafluoroboric acid diethyletherate complex to a solution of alcohol **6b** in Et<sub>2</sub>O resulted in the precipitation of the carbocation salt. The absorption spectrum of  $7b^+BF_4^-$  is almost identical to that  $7b^+CF_3CO_2^-$  formed in situ, but the <sup>1</sup>H NMR spectrum of the tetrafluoroborate salt is significantly broader. Upon addition of [D]TFA to a solution of  $7b^+BF_4^-$  in CDCl<sub>3</sub>, the spectrum became identical to that of  $7b^+CF_3CO_2^-$ .

The <sup>1</sup>H NMR spectrum of **7b**<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> showed the presence of only one species. The spectrum was fully assigned by using a range of 2D NMR techniques. In general, the <sup>13</sup>C NMR spectrum of a carbocation provided information on the delocalization of the positive charge, because cationic centers are strongly deshielded, for example, the central carbon of C(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> resonates at  $\delta$ =335 ppm, whereas resonance-stabilized carbocations do not exhibit such extreme chemical shifts.<sup>[13]</sup> Unfortunately, 2D NMR correlation experiments did not allow us to assign all the <sup>13</sup>C resonances of **7b**<sup>+</sup> due to the lack of protons in proximity to the central carbon atoms. A <sup>13</sup>C-enriched analogue of **6b** was synthesized by using labeled methyl benzoate and indole **5b**. The

<sup>13</sup>C-labelled cation **7b**<sup>+</sup> was formed by addition of acid. By comparison of the spectra of naturally abundant and <sup>13</sup>C-enriched alkyne–cyanines, the central labeled carbon was assigned, and also the adjacent carbons through their coupling to the <sup>13</sup>C label. The change in chemical shift between the cation and the precursor alcohol ( $\Delta \delta_{\rm C}$ ) is a useful guide to charge delocalization. Comparison of these shifts with previously reported compounds with similar bridge structures (Table 1) revealed that the extent of charge delocalization in

Table 1. <sup>13</sup>C NMR chemical shifts ( $\delta_{\rm C}$ ) and changes in chemical shift ( $\Delta \delta_{\rm C}$ ) for alkynyl carbocations compared with the corresponding alcohol precursors, at carbon centers 1–3.

Cation	$\delta_{ m C1}~(\Delta\delta_{ m C1})$	$\delta_{ m C2}\left(\Delta\delta_{ m C2} ight)$	$\delta_{ m C3}\left(\Delta\delta_{ m C3} ight)$	Reference
7b+	139.0 (72.4)	117.2 (25.2)	134.5 (54.6)	this work
8+	162.2 (96.4)	106.5 (17.4)	145.5 (60.6)	[8]
9+	133.9 (66.3)	118.9 (22.8)	136.1 (49.5)	[14]



indole-terminated alkyne–cyanine  $7b^+$  is much greater than in a simple dialkynyl cation  $8^+$  and similar to the porphyrin dimer  $9^+$ , despite the much smaller size of the  $\pi$  system in  $7b^+$ .<sup>[8,14]</sup> The observation that the <sup>13</sup>C chemical shift is greater on C1 than C2 or C3 indicates that C1 has the greatest positive charge in  $7b^+$  and  $8^+$ ; however, localization on C1 is substantially less in  $7b^+$  than in  $8^+$ .

The alkyne-cyanines 7a and b are terminated with 3-indole electron donors. Most previously reported indolebased cyanines are connected at the second position of the indole, although a few examples of trimethine-cyanines substituted at the third position have been reported.<sup>[15]</sup> To ensure proper comparisons, we set out to synthesize a threesubstituted pentamethine reference compound with a central phenyl group (Scheme 2). Vilsmeier formylation<sup>[16]</sup> of 2-phenyl indole and N-methylation gave aldehyde 11, which was transformed to vinyl bromide **12** by a Wittig coupling,<sup>[17]</sup> giving a mix of cis- and trans-isomers in a 1:2 ratio. Halogen-lithium exchange and subsequent trapping with methyl benzoate gave alcohol 13 in poor yields (it is essential to keep the reaction mixture cold during this step; at temperatures above -78 °C, 12 undergoes elimination to give 5b, leading to formation of the acetylene-cyanine precursor 6b as an inseparable by-product). Evidence for the trans, trans-



Scheme 2. Synthesis of reference cation  $14^+$ : a) POCl<sub>3</sub>, DMF, 40 °C, 89%; b) MeI, NaH, DMF, 99%; c) BrCH<sub>2</sub>PPh<sub>3</sub>Br, KOtBu, THF, 81%; d) *n*BuLi, PhCO<sub>2</sub>Me, THF, -78 °C, 5%; e) CF<sub>3</sub>CO<sub>2</sub>H, CHCl<sub>3</sub>.

stereochemistry of **13** was provided by its simple <sup>1</sup>H NMR spectrum and J = 16 Hz coupling constant.

The linear absorption spectrum of the alkene-linked cation  $14^+$  showed an 80 nm blueshift from the alkyne-linked cation  $7b^+$  (Table 2). The absorption maxima of  $7b^+$ 

Table 2. Linear and nonlinear optical properties of cations  $7b^+CF_3CO_2^$ and  $14^+CF_3CO_2^-$  (in CHCl<sub>3</sub>/2 % TFA), and cyanines  $16^+I^-$  and  $17^+I^-$  (in CH<sub>2</sub>Cl<sub>2</sub>). The nonlinear optical properties were measured by the Z-scan method at  $\lambda = 1300$  nm.

Dye	$\lambda_{\max}$ [nm]	$\varepsilon \left[ M^{-1} cm^{-1} \right]$	$\operatorname{Re}(\gamma)^{[a]} [\operatorname{esu}]^{[b]}$	$ \text{Re}(\gamma)/\text{Im}(\gamma) ^{[a]}$
7b+	785	76000	$-1.0 \times 10^{-33}$	1.5
14+	704	69 000	$-2.3 \times 10^{-33}$	1.0
16+	652	220 000	NA <sup>[c]</sup>	NA <sup>[c]</sup>
17*	756	320 000	$-8.4 \times 10^{-33}$	2.1

[a] Errors for Re( $\gamma$ ) were estimated to be  $\pm 10\%$ ; errors for  $|\text{Re}(\gamma)/\text{Im}(\gamma)|$  were estimated to be  $\pm 14\%$ . [b] 1 esu = 1 cm<sup>2</sup> stat Volt<sup>-2</sup>. [c] No closed-aperture signal was measured, thus, Re( $\gamma$ ) was found to be negligible.

and  $14^+$  ( $\lambda = 785$  and 704 nm) are similar to those of the known second-position-linked indocyanine dyes ( $\lambda = 652$  for Cy5 16<sup>+</sup> and 756 nm for Cy7 17<sup>+</sup>; structures are shown in Figure 3). However, the molar extinction coefficients of the new cations are much lower than the two cyanines (Table 2), as was reported for similar third-position-substituted indocyanine dyes.<sup>[15c]</sup>

The NLO properties of the chromophores were also investigated. The real part of  $\gamma$ ,  $\text{Re}(\gamma)$ , and its ratio to the imaginary part of  $\gamma$ ,  $|\text{Re}(\gamma)/\text{Im}(\gamma)|$  were determined at  $\lambda = 1300 \text{ nm}$  by using the femtosecond-pulsed Z-scan technique (results are summarized in Table 2).<sup>[12]</sup> The values of  $\text{Re}(\gamma)$  for nearly all the compounds exhibited characteristics that are typical of cyanines: they are large in magnitude and negative in sign. Although this was expected for the second-and third-position-substituted indocyanines, observation of similar characteristics for **7b**<sup>+</sup> is entirely consistent with the theoretical results<sup>[5]</sup> that showed model alkyne-carbocations



Figure 3. Structures of cyanines  $16^+$  and  $17^+$ , and triarylmethyl cations crystal violet  $18^+$  and brilliant green  $19^+$  used as reference compounds for 2PA.

exhibited cyanine-like properties. On the contrary, it should be noted that  $16^+$  exhibited an unexpectedly low (negligible) value of Re( $\gamma$ ) at  $\lambda = 1300$  nm. To rationalize this result, it is important to note that the value of  $\operatorname{Re}(\gamma)$  can undergo significant dispersion near a 2PA resonance. On the highenergy side of the resonance, a strong negative dip in  $\text{Re}(\gamma)$ occurred, whereas on the low-energy side, there was a strong positive peak. The 2PA spectrum of  $16^+$  showed that excitation at  $\lambda = 1300$  nm, which is on the low energy side of the 2PA resonance (see below). This leads to reduction of the expected large, negative,  $Re(\gamma)$  by the competing positive dispersion peak, leading to the negligible value of  $\operatorname{Re}(\gamma)$  observed by Z-scan measurements. The 2PA spectra of the remaining compounds indicated that 1300 nm resides on the high-energy side of the 2PA resonance. Consequently, one would expect enhancements of the intrinsic, negative  $Re(\gamma)$  values. This is consistent with results from a simplified two-state model for zero-frequency  $\operatorname{Re}(\gamma)$ ,<sup>[3]</sup> in which one would expect that the carbocations  $(7b^+ \text{ and } 14^+)$ , given their weaker  $\varepsilon$  values, should possess  $\operatorname{Re}(\gamma)$  values with significantly smaller magnitudes than cyanines 16<sup>+</sup> and 17<sup>+</sup>. Instead, comparable values of  $\operatorname{Re}(\gamma)$  were observed for the carbocations due to this two-photon-dispersion enhancement.

Nondegenerate two-photon absorption (ND-2PA) spectra of cations **7b**<sup>+</sup>, **14**<sup>+</sup>, **16**<sup>+</sup>, **17**<sup>+</sup>, **18**<sup>+</sup>, and **19**<sup>+</sup> were recorded by using an ultrafast pump-probe spectroscopy set-up. The ND-2PA spectra are shown in Figures 4, 5, and 6, overlaid with the normalized one-photon absorption (1PA) spectra. This technique probes 2PA by combining a tunable pump pulse (120 fs,  $\lambda = 700-2200$  nm) with a broadband white-light continuum probe pulse ( $\lambda = 420-850$  or 850–1650 nm, latter designated as NIR).<sup>[12]</sup> The sum of the photon energies from the two pulses allowed access to relevant two-photon transitions. The broadband nature of the probe pulse, coupled with the use of different pump wavelengths (shown in the legends) allowed coverage of the entire 2PA spectrum. The abscissa in each figure reflects the combined photon energinated photon energinated photon energinated spectrum.



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Figure 4. ND-2PA spectra (circles) of cyanines  $16^+I^-$  (top) and  $17^+I^-$  (bottom) recorded in  $CH_2Cl_2$ . The legend gives the pump wavelength employed. The solid lines show the 1PA spectra. The crosses show the degenerate 2PA cross-sections determined by Z-scan.

gies of the two beams involved in the 2PA process, to give an overall transition wavelength. The left ordinate denotes  $(1 \text{ GM} = 1 \times$ the ND-2PA cross-section,  $\delta_{
m ND}$  $10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>). The sharp peaks in these ND-2PA spectra are due to inverse Raman scattering present in the solvent and chromophore; however, these signatures are spectrally narrow and therefore distinguishable from the broadband ND-2PA response. The ND-2PA technique was chosen, because it provides rapid and broadband characterization and is amenable for studying nonfluorescent samples. However, for comparison purposes, degenerate 2PA (D-2PA) cross-sections ( $\delta_{\rm D}$ ) at selected wavelengths were determined from open-aperture Z-scans and two-photon-induced fluorescence (2PF).<sup>[12]</sup> These values (right ordinates), also shown in Figures 4-6, indicate that there is good agreement between the three methods.

The ND-2PA spectra of  $16^+$  and  $17^+$  illustrate a number of characteristics typical for polymethine–cyanines (Figure 4). First, the lower energy 2PA peak is spectrally coincident with a vibronic shoulder of the lowest energy onephoton state at  $E_{10}$ . The vibronic coupling of the lowestlying 1PA-active state appears to be fairly strong, as has been observed both in other cyanines (experimentally<sup>[3,18]</sup> and theoretically<sup>[18b]</sup>) and in squaraines (experimentally<sup>[19]</sup>

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Figure 5. ND-2PA spectra (circles) of triarylmethyl carbocations crystal violet  $18^+$ Cl<sup>-</sup> (top) and brilliant green  $19^+$ HSO<sub>4</sub><sup>-</sup> (bottom) recorded in MeCN. The legend gives the pump wavelength employed. "NIR" refers to use of the near-infrared probe region. The solid lines show the 1PA spectra. The crosses show the degenerate 2PA cross-sections determined by two-photon-excited fluorescence.

and theoretically<sup>[20]</sup>). Second, higher-energy 2PA peaks were observed at approximately  $1.7 \times E_{10}$ , again typical for previously investigated cyanines.<sup>[3,18a]</sup> The ND-2PA spectrum of the alkene-bridge model carbocation **14**<sup>+</sup> was found to be similar to that of these cyanines (Figure 6) with pronounced vibronically allowed 2PA lying at approximately 1200 cm<sup>-1</sup> above the lowest lying 1PA-active state. Some difficulties encountered with absorption of shorter wavelength pump beams prohibited access to the higher-energy 2PA bands for this compound.

The carbocation  $7b^+$  may be considered as an extended version of triarylmethyl carbocations, such as brilliant green  $19^+$  and crystal violet  $18^+$  (Figure 3) with the latter possessing a higher degree of symmetry. The 2PA spectra of  $18^+$ and  $19^+$  have been previously calculated, and the D-2PA cross-sections were measured by 2PF at selected wavelengths.<sup>[21]</sup> The reported cross-sections are shown in Figure 5 as crosses, together with the broadband 2PF data for Brilliant Green  $19^+$  from the current study (2PF data could not be obtained for  $18^+$  due to the very low quantum yield.) The ND-2PA spectra of  $18^+$  and  $19^+$  agree well with the 2PF data from this work and Ref. [21]. To the best of our



Figure 6. ND-2PA spectra (circles) of carbocations  $7b^+CF_3CO_2^-$  (top) and  $14^+CF_3CO_2^-$  (bottom) recorded in CHCl<sub>3</sub>/2% TFA. The legend gives the pump wavelength employed. The solid lines show the 1PA spectra. The crosses show the degenerate 2PA cross-sections determined by Z-scan.

knowledge, this represents the first experimental measurement of broadband 2PA spectra for these known octupolar molecules, and it reveals a number of interesting spectral characteristics. In particular, the longest wavelength 2PA band is coincident with the lowest-energy one-photon state at  $E_{10}$  (e.g., for **19<sup>+</sup>** this occurs at  $\lambda \approx 630$  nm), consistent with the fact that both one- and two-photon transitions into this 1E' state are allowed in these compounds.<sup>[21]</sup> Additionally, the short wavelength 2PA peaks are associated with the 2A' excited states in these compounds and occur at slightly lower energy than for cyanines ( $\approx 1.5 \times E_{10}$ ). It is also interesting to note that in the 2PF spectra vibronically allowed 2PA is observed into  $E_{10}$  (e.g., for 19<sup>+</sup> this occurs at  $\approx$  575 nm) as in cyanines, albeit with a reduced response (unfortunately, in the case of  $18^+$ , the vibronic 2PA is not clearly discernible in the ND-2PA spectrum). This twophoton response has been predicted theoretically for crystal violet 18<sup>+</sup> and the experimentally determined dispersion of the first hyperpolarizability has also supported such vibronic activity.<sup>[21]</sup> The ND-2PA spectrum of the alkyne carbocation  $7b^+$  exhibits all the spectral characteristics described above for the triarylmethyl carbocations, particularly for brilliant green (19<sup>+</sup>), the compound with reduced symmetry

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(Figure 6). It is also interesting to note that the vibronically allowed 2PA for  $7b^+$  lies at approximately 1700 cm<sup>-1</sup> above the lowest lying 1PA active state, as was expected for an alkyne-bridged system, in contrast to the alkene-bridged polymethines or aryl-bridged octupolar molecules.

Quantum chemical calculations were performed on the alkene/alkyne carbocations to help rationalize and corroborate the observations reported above.<sup>[12]</sup> In quadrupolar and octupolar compounds, which consist of a combination of electron donor (D) and acceptor (A) segments, two-photon cross-sections are enhanced with electron-density shift between the D- $\pi$ -A moieties. Beljonne et al. underlined that the increase in the cross-sections of octupolar compounds are accounted for by donor-to-acceptor charge transfer in the three arms.<sup>[22]</sup> Figure 7 illustrates the calculated charge



Figure 7. Illustration of the charge transfer occurring upon excitation from the  $S_0$  ground state to the strongly 2PA-active state of  $7b^+$  ( $S_2$ ),  $14^+$  ( $S_2$ ),  $18^+$  ( $S_3$ ), and  $19^+$  ( $S_2$ ) at the INDO/MRDCI level. Open circles denote the loss of charge and filled circles the gain of charge upon photo-excitation.

transfer that occurs upon going from the ground state to the excited state with high 2PA response ( $S_2$  or  $S_3$  state in Table 3) for cations **7b<sup>+</sup>**, **14<sup>+</sup>**, **18<sup>+</sup>**, and **19<sup>+</sup>**. As in cations **18<sup>+</sup>** and **19<sup>+</sup>**, the planar arrangement of **7b<sup>+</sup>** allows charge transfer between each of the three aromatic arms. However, there is no charge transfer taking place along the phenyl

Table 3. Electronic and optical properties of  $7b^+$ ,  $14^+$ ,  $18^+$ , and  $19^+$  calculated at the INDO/MRDCI//SOS level.

	S <sub>n</sub>	E [eV]	f	$\mu_{0n}$ [D]	$\mu_{1n}$ [D]	$\delta$ [GM]
7b+	$S_1$	1.65	0.99	12.6	_	32
	$S_2$	2.55	0.15	3.9	8.4	$2.5 \times 10^{3}$
14+	$S_1$	1.43	1.21	14.9	-	11
	$S_2$	2.72	0.04	2.0	8.2	$1.1 \times 10^{5}$
18+	$S_1$	1.90	0.48	8.2	-	78
	$S_2$	1.98	0.49	8.0	-	97
	$S_3$	3.60	0.01	0.0	$(\mu_{13}/\mu_{23})$ 7.5/7.9	$1.0 \times 10^{5}$
19+	$S_1$	1.84	0.74	10.3	-	27
	$S_2$	2.80	0.31	5.4	9.0	$1.7 \times 10^{3}$

arm of 14<sup>+</sup>, because it is twisted out of plane by about 55°; this implies that the phenyl substituent makes a small contribution to the 2PA response of 14<sup>+</sup>. The S<sub>3</sub> state of 18<sup>+</sup> is very weakly active (likely, vibronically allowed) in 1PA, but is strongly 2PA active, whereas the charge transfer (S<sub>2</sub>) states of 7b<sup>+</sup> and 19<sup>+</sup> are both 1PA and 2PA active, as was seen in the UV/Vis and ND-2PA spectra, due to greater lowering of the symmetry in 7b<sup>+</sup> and 19<sup>+</sup> relative to 18<sup>+</sup>.

Finally, we note that it was shown earlier in the case of squaraine compounds that the lowest-energy 2PA activity was not related to the presence of a 2PA-active electronic state; rather, it could be explained through coupling of the 1PA-active  $S_1$  state of these compounds with b(u) vibrational modes.<sup>[20,23]</sup> For the model cyanine and alkyne–cyanine structures reported herein, the ND-2PA spectra exhibited significant low-lying 2PA activity some 0.2–0.25 eV above the lowest 1PA-active state ( $S_1$ ), which is at a much lower energy than the one calculated for the lowest-energy strongly active 2PA state. These results strongly suggest that the lowest-energy 2PA activity in the present model compounds has also a vibronic origin.

# Conclusion

The alkyne-linked cyanine analogue  $7b^+$  was synthesized and found to be sufficiently stable for spectroscopic analysis under ambient conditions. Despite possessing a large bondlength alternation, the compound exhibited characteristics indicative of traditional cyanines. Absorption spectroscopy showed a strong near-IR band at  $\lambda = 785$  nm and a weaker visible band at 550 nm. The extinction coefficient of the near-IR band is smaller than for a typical cyanine (such as  $16^+$  or  $17^+$ ), but comparable to previously reported indolium dyes substituted on the third position. <sup>13</sup>C NMR spectroscopy of an isotopically enriched cation was used to investigate the extent of delocalization across the alkynyl bridge. The change in chemical shift upon cation formation indicated a large degree of charge delocalization, comparable to that in the previously reported porphyrin cation  $9^+$ .

A vinylene-linked 3-indole cyanine cation  $14^+$  was synthesized to compare its optical properties with alkyne-cyanine  $7b^+$ . The values of the real part of the third-order polarizability, Re( $\gamma$ ), for  $14^+$  and  $7b^+$  are comparable to those of traditional cyanines, particularly when accounting for twophoton dispersion enhancement effects. ND-2PA measurements confirm that the alkene carbocation  $14^+$  has cyaninelike characteristics, such as vibronically allowed 2PA into the lowest-lying 1PA-active state. On the other hand, the alkyne carbocation  $7b^+$  exhibits characteristics indicative of triarylmethyl carbocation dyes, such as a low-energy 2PA band coincident with a 1PA-allowed transition, similar to the 2PA spectrum of brilliant green ( $19^+$ ).

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# **Experimental Section**

**General**: Reactions were carried out under nitrogen or argon atmospheres, unless otherwise stated. Dry toluene and THF were used after passing through a column of activated alumina. Triethylamine was distilled from  $CaH_2$  prior to use. All other reagents were used as supplied.

Column chromatography was carried out on silica gel 60 under a positive pressure of nitrogen. Ratios are reported by volume when mixtures of solvents were used. NMR spectra were recorded at 300 K on a Bruker DPX400 (400 MHz) or Bruker AVANCE AVC500 (500 MHz) spectrometer. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane. UV/Vis spectra were recorded in solution on a Perkin–Elmer lambda 20 UV/Vis spectrometer. Mass spectra were measured by electrospray ionization time-of-flight (ESI-TOF) by using a Micromass LCT premier spectrometer. Only molecular ions and major peaks are reported.

Synthesis of 3-iodo-1-methyl-2-phenylindole (3b): A one-pot method was adopted by combining published procedures.<sup>[10,24]</sup> 2-Phenylindole (1b; 1.00 g, 5.18 mmol) was dissolved in DMF (40 mL). Ground potassium hydroxide (0.726 g, 12.9 mmol) was added and the solution turned green. A solution of iodine (1.33 g, 5.23 mmol) in DMF (20 mL) was added dropwise, until the brown color persisted. Sodium hydride (60% dispersion, 0.248 g, 6.22 mmol) was added and the mixture stirred for 10 min. Iodomethane (0.946 mL, 6.22 mmol) was added, and the reaction mixture was stirred at 20 °C for 1 h, then quenched with H<sub>2</sub>O (20 mL), extracted with EtOAc (40 mL), and washed with H<sub>2</sub>O ( $3 \times 40$  mL). The solution was dried over magnesium sulfate. Evaporation of the solvents gave the product (1.70 g, 98%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta =$  7.55–7.44 (6H, m), 7.32 (1H, d, J=7.7 Hz), 7.26 (1H, t, J=7.0 Hz), 7.17 (1H, dd, J=7.2, 7.6 Hz), 3.60 ppm (3H, s).

Synthesis of 2-methyl-4-(1-methyl-2-phenyl-indol-3-yl)but-3-yn-2-ol (4b): Sonogashira coupling was achieved by following a published procedure.<sup>[25]</sup> 2-Ph-N-Me iodoindole **3b** (1.78 g, 5.38 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.189 g, 0.270 mmol) and copper(I) iodide (0.102 g, 0.538 mmol) were dried under vacuum. Triethylamine (53 mL) and DMF (35 mL) were added, and the solution was freeze/thaw degassed. 2-Methyl-3-butyn-2-ol (1.04 mL, 10.7 mmol) was added, and the mixture was stirred for 18 h at 20°C. The solvents were removed, and the product purified was by silica chromatography (40-60°C petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub> 20:4:1) to give product as a yellow oil (0.949 g, 61 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.74$  (1 H, d, J = 7.7 Hz), 7.62 (2 H, d, J =7.0 Hz), 7.52 (2 H, dd, J=7.0, 7.9 Hz), 7.45 (1 H, m), 7.37 (1 H, d, J= 8.2 Hz), 7.30 (1 H, dd, J=7.2, 8.0 Hz), 7.23 (1 H, dd, J=7.5, 7.8 Hz), 3.75 (3H, s), 1.59 ppm (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta = 143.8$ , 137.1, 130.7, 130.1, 128.8, 128.5, 128.4, 128.3, 122.8, 120.7, 119.8, 109.7, 96.0, 76.5, 66.0, 31.7, 29.1 ppm; HRMS (ESI): m/z calcd for C<sub>20</sub>H<sub>19</sub>NNaO: 312.1357 ([*M*]<sup>+</sup>); found: 312.1359.

Synthesis of 3-ethynyl-1-methyl-2-phenyl-indole (5b): Removal of the protecting group was achieved by adapting a published procedure.<sup>[26]</sup> Protected acetylene indole **4b** (0.450 g, 1.55 mmol) was dissolved in toluene (75 mL), and freshly ground sodium hydroxide (1.24 g, 31.1 mmol) was added. The mixture was stirred at reflux for 18 h. The solvents were removed, and the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL), washed with water (3×40 mL), and dried over magnesium sulfate. After purification by silica chromatography (40–60 °C petroleum ether/NEt<sub>3</sub> 1:0.05) and evaporation of solvents, the product was obtained as a pale yellow oil (0.140 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.74 (1H, d, *J*=7.8 Hz), 7.62 (2H, d, *J*=7.0 Hz), 7.52 (2H, dd, *J*=7.2, 8.0 Hz), 7.45 (1H, m), 7.37 (1H, d, *J*=8.2 Hz), 7.30 (1H, dd, *J*=7.5, 7.0 Hz), 7.23 (1H, dd, *J*=7.0, 7.7 Hz), 3.75 (3H, s), 3.15 ppm (1H, s).

Synthesis of 2-phenyl acetylene–cyanine alcohol (6b): Deprotected acetylene indole 5b (0.140 g, 0.606 mmol) was dissolved in THF (45 mL), and the solution was freeze/thaw degassed. Methyl benzoate (0.038 mL, 0.30 mmol) and lithium bis(trimethylsilyl)amide (1.0 m in THF, 2.42 mL) were added, and the solution was stirred at 20 °C for 1 h. The reaction was quenched with saturated aqueous solution of NH<sub>4</sub>Cl (10 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL), and washed with H<sub>2</sub>O ( $2 \times 20 \text{ mL}$ ). Purifica-

tion by silica chromatography (40–60 °C petroleum ether/NEt<sub>3</sub> 1:0.02) and removal of solvents gave the product (0.164 g, 95%) as a yellowbrown solid. M.p. 70–76 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.81–7.78 (4H, m), 7.61 (4H, d, *J*=8.3 Hz), 7.47–7.38 (8H, m), 7.34–7.30 (5H, m), 7.25 (2H, dd, *J*=6.9, 7.8 Hz), 3.76 ppm (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 142.7, 137.1, 130.6, 130.2, 129.0, 128.5, 128.4, 128.1, 128.1, 126.2, 122.9, 120.9, 120.2, 109.8, 95.8, 91.9, 79.9, 66.7, 31.6 ppm; HRMS (ESI): *m/z* calcd for C<sub>41</sub>H<sub>30</sub>N<sub>2</sub><sup>+</sup>: 549.2325 ([*M*]<sup>+</sup>); found: 549.2328.

**Synthesis of 2-phenyl acetylene–cyanine trifluoroacetate (7b<sup>+</sup>)**: The acetylene–cyanine was formed in situ for NMR and absorption experiments by addition of trifluoroacetic acid (2% by volume with respect to solvent) to a solution of the alcohol precursor **6b** in CHCl<sub>3</sub>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/2% [D]TFA):  $\delta$ =7.84 (2H, d, *J*=6.9 Hz), 7.81 (2H, dd, *J*=7.1, 6.9 Hz), 7.72–7.77 (8H, m), 7.55–7.64 (9H, m), 7.34 (2H, dd, *J*=7.9, 7.7 Hz), 3.97 ppm (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/2% [D]TFA):  $\delta$ =156.9, 139.1, 139.0, 136.0, 135.3, 134.5, 131.6, 130.8, 130.7, 129.4, 129.4, 128.0, 127.8, 127.0, 125.6, 121.2, 117.8, 117.2, 115.6, 113.3, 112.3, 111.0, 101.4, 99.9, 33.0 ppm; UV/Vis (CHCl<sub>3</sub>/2% TFA):  $\lambda_{max}$  (log ε)=536 (4.20), 785 nm (4.88).

Synthesis of 2-phenyl-1-methylindole-3-carbaldehyde (11): Formyl indole was methylated following a published procedure.<sup>[24]</sup> Sodium hydride (60% dispersion in oil, 0.022 g, 0.54 mmol) was added to formyl indole 10 (0.100 g, 0.45 mmol) in DMF (2 mL) and stirred for 10 min. Iodomethane (0.082 mL, 0.54 mmol) was added and the reaction mixture and stirred for 1 h. H<sub>2</sub>O (2 mL) was added to quench the reaction, and the product was extracted with EtOAc (10 mL), washed with H<sub>2</sub>O (2×10 mL), and dried over magnesium sulfate. Evaporation of solvents gave the product as a yellow powder (0.104 g, 99%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.96 (1H, s), 8.23 (1H, d, *J* = 7.7 Hz), 7.60–7.69 (7H, m), 7.39 (1H, dd, *J* = 7.0, 8.2 Hz), 7.33 (1H, dd, *J* = 7.8, 7.2 Hz), 3.70 ppm (3H, s); HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>13</sub>NNaO: 258.0889 ([*M*]<sup>+</sup>); found: 258.0890.

Synthesis of 3-(2-bromovinyl)-1-methyl-2-phenyl-indole (12): Wittig coupling was carried out following a published procedure.<sup>[17]</sup> A solution of potassium *tert*-butoxide (0.334 g, 2.98 mmol) in THF (5 mL) was added to a solution of (bromomethyl)triphenylphosphonium bromide (1.30 g, 2.98 mmol) in THF (10 mL) at -78 °C. The resulting yellow solution was added to formyl indole 11 (0.200 g, 0.85 mmol) in THF (20 mL) and stirred for 2 h at 20 °C. The reaction was quenched with H<sub>2</sub>O (5 mL), extracted with CHCl<sub>3</sub> (20 mL), and washed with H<sub>2</sub>O (2 × 20 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 5:1) to give a colorless oil (0.215 g, 81 %), which was a mixture of the *cis*- and *trans*-isomers in a 1:2 ratio. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.85 (indole-H, *trans*-isomer, *J*=7.5 Hz), 7.07 (CC-H, *trans*-isomer, *J*=14.2 Hz), 6.73 (CC-H, *trans*-isomer, *J*=14.2 Hz), 6.39 ppm (CC-H, *cis*-isomer, *J*=7.5 Hz).

Synthesis of 2-phenyl cyanine alcohol (13): nBuLi(1.6 m in hexanes, 0.400 mL, 0.641 mmol) was added to a solution of bromovinvlindole 12 (mixed isomers) (0.200 g, 0.641 mmol) in THF (20 mL) at -78 °C. After 10 min, methyl benzoate (0.400 mL, 3.20 mmol) was added over 5 min, and the solution was stirred for 1 h at -78 °C. The reaction was quenched with H<sub>2</sub>O (5 mL), the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with H<sub>2</sub>O (3×20 mL). The mixture was purified by column chromatography (40-60 °C petroleum ether/CH2Cl2/NEt3 6:1:0.1) to give the product (8.9 mg, 5%) as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.88$  (2H, d, J = 8.0 Hz), 7.54 (2H, dd, J = 8.5, 1.4 Hz), 7.35-7.44 (13H, m), 7.28-7.32 (4H, m), 7.17-7.23 (3H, m), 6.74 (2H, d, J= 16.2 Hz), 6.61 (2H, d, J=16.2 Hz), 3.62 ppm (6H, s); <sup>13</sup>C NMR  $(125 \text{ MHz}, \text{ CDCl}_3): \delta = 146.0, 140.3, 137.7, 132.0, 131.2, 130.9, 128.4,$ 128.3, 128.0, 126.8, 126.4, 125.7, 122.5, 122.2, 120.5, 120.4, 111.0, 109.6, 78.4, 46.1, 31.0, 29.7 ppm; HRMS (ESI): m/z calcd for C41H34N2O 570.72 ([*M*]<sup>+</sup>; calcd for -OH: 553.26); found: 553.26.

Synthesis of 2-phenyl cyanine trifluoroacetate ( $14^+$  CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>): The cyanine was formed in situ for NMR and absorption experiments by addition of trifluoroacetic acid (2% by volume with respect to solvent) to a solution of the alcohol precursor **13** in CHCl<sub>3</sub>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/2% [D]TFA):  $\delta$ =8.19 (2H, bs), 7.65 (2H, d, *J*=14.5 Hz), 7.53–

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7.60 (8H, m), 7,48 (4H, dd, J=7.5, 7.2 Hz), 7.37-7.42 (3H, m), 7.32 (3H, m), 7.28 (1H, s), 7.18 (2H, bs), 3.80 ppm (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/2% [D]TFA): δ=156.5, 139.7, 131.0, 130.4, 129.7, 128.9, 128.3, 126.9, 126.5, 125.5, 124.9, 122.1, 118.7, 112.0, 46.8, 32.6, 29.7 ppm; UV/Vis (CHCl<sub>3</sub>/2 % TFA):  $\lambda_{max}$  (log  $\varepsilon$ ) 436 (3.59), 704 nm (4.84).

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- [1] L. A. Ernst, R. K. Gupta, R. B. Mujumdar, A. S. Waggoner, Cytometrv 1989, 10, 3-10.
- [2] M. Emmelius, G. Pawlowski, H. W. Vollmann, Angew. Chem. 1989, 101, 1475-1502; Angew. Chem. Int. Ed. Engl. 1989, 28, 1445-1471.
- [3] J. M. Hales, J. Matichak, S. Barlow, S. Ohira, K. Yesudas, J.-L. Brédas, J. W. Perry, S. R. Marder, Science 2010, 327, 1485-1488.
- [4] S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas, B. M. Pierce, Science 1994, 265, 632-635.
- [5] S. Ohira, J. M. Hales, K. J. Thorley, H. L. Anderson, J. W. Perry, J.-L. Brédas, J. Am. Chem. Soc. 2009, 131, 6099-6101.
- D. Jacquemin, J. Phys. Chem. A 2011, 115, 2442-2445.
- [7] S. Nakatsuji, K. Nakashima, K. Yamamura, S. Akiyama, Tetrahedron Lett. 1984, 25, 5143-5146.
- [8] K. Komatsu, T. Takai, S. Aonuma, K. Takeuchi, Tetrahedron Lett. 1988, 29, 5157-5160.
- [9] C. Arisandy, E. Fullam, S. Barlow, J. Organomet. Chem. 2006, 691, 3285-3292.
- [10] H. P. Xia, W. F. Wu, W. S. Ng, I. D. Williams, G. Jia, Organometallics 1997, 16, 2940-2947.
- [11] V. Bocchi, G. Palla, Synthesis 1982, 1096-1097.
- [12] For details, see the Supporting Information.
- [13] a) G. A. Olah, Angew. Chem. 1995, 107, 1519-1532; Angew. Chem. Int. Ed. Engl. 1995, 34, 1393-1405; b) G. A. Olah, R. J. Spear, P. W. Westerman, J. M. Denis, J. Am. Chem. Soc. 1974, 96, 5855-5859.

[14] K. J. Thorley, J. M. Hales, H. L. Anderson, J. W. Perry, Angew. Chem. 2008, 120, 7203-7206; Angew. Chem. Int. Ed. 2008, 47, 7095-7098.

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- [15] a) T. N. Galiullina, P. I. Abramenko, A. V. Kazymov, V. M. Gorokhovskii, Chem. Heterocycle Compd. 1981, 17, 790-794; b) T. M. Karymova, P. I. Abramenko, L. G. Kurkina, Chem. Heterocycle Compd. 1988, 24, 736-740; c) M. Van der Auweraer, M. Van den Zegel, N. Boens, F. C. De Schryver, F. Willig, J. Phys. Chem. 1986, 90, 1169-1175.
- [16] G. F. Smith, J. Chem. Soc. 1954, 3842-3846.
- [17] D. P. Arnold, R. D. Hartnell, Tetrahedron 2001, 57, 1335-1345.
- [18] a) J. Fu, L. A. Padilha, D. J. Hagan, E. W. Van Stryland, O. V. Przhonska, M. V. Bondar, Y. L. Slominsky, A. D. Kachkovski, J. Opt. Soc. Am. A J. Opt. Soc. Am. B. 2007, 24, 56-66; b) F. Terenziani, O. V. Przhonska, S. Webster, L. A. Padilha, Y. L. Slominsky, I. G. Davydenko, A. O. Gerasov, Y. P. Kovtun, M. P. Shandura, A. D. Kachkovski, D. J. Hagan, E. W. Van Stryland, A. Painelli, J. Phys. Chem. Lett. 2010, 1, 1800-1804.
- [19] D. Scherer, R. Dorfler, A. Feldner, T. Vogtmann, M. Schwoerer, U. Lawrentz, W. Grahn, C. Lambert, Chem. Phys. 2002, 279, 179-207.
- [20] S. Ohira, I. Rudra, K. Schmidt, S. Barlow, S.-J. Chung, Q. Zhang, J. Matichak, S. R. Marder, J.-L. Brédas, Chem. Eur. J. 2008, 14, 11082-11091
- [21] D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder, J.-L. Brédas, Adv. Funct. Mater. 2002, 12, 631-641.
- [22] J. Campo, A. Painelli, F. Terenziani, T. Van Regemorter, D. Beljonne, E. Goovaerts, W. Wenseleers, J. Am. Chem. Soc. 2010, 132, 16467-16478.
- [23] F. Terenziani, A. Painelli, C. Katan, M. Charlot, M. Blanchard-Desce, J. Am. Chem. Soc. 2006, 128, 15742-15755.
- Y. Nakao, K. S. Kanyiva, S. Oda, T. Hiyama, J. Am. Chem. Soc. [24] 2006, 128, 8146-8147.
- [25] B. Witulski, J. R. Azcon, C. Alayrac, A. Arnautu, V. Collot, S. Rault, Synthesis 2005, 771-780.
- [26] C. Wang, L.-O. Palsson, A. S. Batsanov, M. R. Bryce, J. Am. Chem. Soc. 2006, 128, 3789-3799.

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