DOI: 10.1002/asia.201402896

trans/cis-Isomerization of Fluorene-Bridged Azo Chromophore with Significant Two-Photon Absorbability at Near-Infrared Wavelength

Chih-Chien Chu,*^[a, b] Ya-Chi Chang,^[a] Bo-Kai Tsai,^[c] Tzu-Chau Lin,^[c] Ja-Hon Lin,^[d] and Vincent K. S. Hsiao^[e]

Abstract: Azo-containing materials have been proven to possess second-order nonlinear optical (NLO) properties, but their third-order NLO properties, which involves twophoton absorption (2PA), has rarely been reported. In this study, we demonstrate a significant 2PA behavior of the novel azo chromophore incorporated with bilateral diphenylaminofluorenes (DPAFs) as a π framework. The electrondonating DPAF moieties cause a redshifted π - π * absorption band centered at 470 nm, thus allowing efficient blue-lightinduced trans-to-cis photoisomerization with a rate constant of 2.04×10^{-1} min⁻¹ at the photostationary state (PSS). The open-aperture Z-scan technique that adopted a femtosecond (fs) pulse laser as excitation source shows an appreciably higher 2PA cross-section for the fluorene-derived azo chromophore than that for common azobenzene dves at near-infrared wavelength ($\lambda_{ex} = 800$ nm). Furthermore, the fs 2PA response is quite uniform regardless of the molecular geometry. On the basis of the computational modeling, the intramolecular charge-transfer (ICT) process from peripheral diphenylamines to the central azo group through a fluorene π bridge is crucial to this remarkable 2PA behavior.

Azobenzene (azo) chromophores have been incorporated into a wide variety of molecular architectures including polymers, dendrimers, liquid crystals, self-assembled monolayers, and biomaterials.^[1] Azo chromophores undergo a uniquely clean and efficient photoisomerization; they ex-

- [b] Prof. Dr. C.-C. Chu Department of Medical Education Chung Shan Medical University Hospital, Taichung 40201 (Taiwan)
- [c] B.-K. Tsai, Prof. Dr. T.-C. Lin Department of Chemistry National Central University, Jhong-Li 32001 (Taiwan)

 [d] Prof. Dr. J.-H. Lin Department of Electro-Optical Engineering National Taipei University of Technology, Taipei 10608 (Taiwan)

- [e] Prof. Dr. V. K. S. Hsiao Department of Applied Materials and Optoelectronic Engineering National Chi Nan University, Puli 54561 (Taiwan)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201402896.

hibit facile geometric isomerization between their trans and *cis* forms.^[2] Generally, *trans*-azobenzene shows intense $\pi - \pi^*$ absorption in the UV region, and noncoherent UV light can rapidly induce the trans-to-cis isomerization. The cis isomer has an enhanced $n-\pi^*$ absorption in the visible region; thus, the trans isomers are regenerated from the cis state through visible-light irradiation. Accordingly, trans/cis azobenzenes can be readily switched by alternating UV and visible-light exposure. This light-induced interconversion allows the system that incorporates azo chromophores to be applied in phototriggered molecular switches and machines.^[3] With electron donor-acceptor (D-A) ring substitution, azo chromophores have been extensively studied for second-order nonlinear optical (NLO) applications.^[4] Irradiation in the absorption band of poled azo polymers with a pulse laser beam, for example, can cause significant second-harmonic generation (SHG) decay correlated with trans-to-cis isomerization, followed by a rapid recovery to the initial SHG level when the *cis* isomer thermally relaxes back to the *trans* state.^[5] This marked photoswitching of the "on/off" SHG signal is mainly attributed to the distinctive hyperpolarizability of *trans* and *cis* azobenzenes. A more π -conjugated trans isomer has a higher hyperpolarizability, thus enabling the NLO response to be more readily switched between the trans and cis states.

Recently, third-order NLO behavior that involves a twophoton absorption (2PA) process has drawn considerable attention because of many promising applications in the emerging fields of photonics and biophotonics, including optical power limiting, 3D data storage, 3D microfabrication, bioimaging and tracking, and 2PA-assisted photodynamic therapy.^[6] The 2PA efficiency, namely, the 2PA cross-section for the organic chromophores, is, in general, closely related to both the intramolecular charge-transfer (ICT) efficiency in D- π -D-, A- π -A-, and D- π -A-type structures and the effective π -conjugation length within a molecule.^[7] The π bridges, similar to a highly rigid fluorene unit, provide delocalization and conjugation, which are critical for increasing the 2PA cross-section. Moreover, elongation of the π frameworks through either alkenyl (C=C) or alkynyl (C = C) linkages also results in extension of the effective π -conjugation length and, thus, the enhancement of 2PA efficiency. However, use of an azo moiety (N=N) as the conjugation linkage to achieve the 2PA process has been rarely reported.^[8] Antonov et al. conducted a systematic study on the 2PA cross-

Wiley Online Library

 [[]a] Prof. Dr. C.-C. Chu, Y.-C. Chang School of Medical Applied Chemistry, Chung Shan Medical University, South District, Taichung (Taiwan) E-mail: jrchu@csmu.edu.tw

sections in several D– π –A-type azoaromatic compounds and suggested that the strength of the donor and/or acceptor groups is significant.^[8a] Furthermore, Magennis et al. demonstrated a 2PA photochromism in a commercial azo chromophore. The *trans*-to-*cis* isomerization could be performed using two-photon excitation by employing 740 nm femtosecond (fs) laser pulses.^[8b] Consequently, we envisioned that the third-order 2PA behavior of azo-containing materials proven to possess a second-order NLO property should be explored further.

As a proof-of-concept for this study, we synthesized a D- π -D compound 1, in which two electron-donating diphenylaminofluorenes (DPAFs) were directly linked by an azo group, to examine the correlation between trans/cis photoisomerization and 2PA properties. As shown in Scheme 1, symmetric azo compound 1, indicated in deep orange, was successfully synthesized by homocoupling two 2-amino-substituted DPAF through a copper-catalyzed aerobic oxidative dehydrogenative process.^[9] This symmetric azo-coupling reaction was executed under mild conditions, using copper bromide as the catalyst and air as the oxidant. The excellent yield in this reaction was attributed to the electron-donating character of the diphenylamine substituents. Thin-layer chromatography (TLC) analysis, using an ethyl acetate and hexane mixture (1:19) as the eluent, showed a single composition for compound 1 at $R_{\rm f}=0.83$, thus indicating clearly a geometric state of either pure *trans* or pure *cis* form. The proton and carbon peaks shown in the ¹H and ¹³C NMR spectra also confirmed the existence of compound 1 as



Scheme 1. Synthetic route for azo compound 1 bearing bilateral electron-donating diphenylaminofluorenes (DPAFs).

a single component (see the Supporting Information). However, neither method could determine the *trans* and *cis* geometries. Research has shown that *trans* and *cis* azobenzenes can be distinguished according to their characteristic Raman shifts.^[10] Therefore, we adopted micro-Raman spectroscopy to analyze directly the vibrational spectrum of a solid sample. Figure 1a shows the Raman spectra for compound **1** based on using a 633 nm He:Ne laser as the excitation source. The Raman shifts centered at 1142 (CN stretch),



Figure 1. a) Micro-Raman spectroscopic analysis for azo compound 1. The marked peaks denote the characteristic vibration modes of the *trans* isomer. b) UV-visible spectroscopic analysis for *trans* 1 upon 466 nm LED irradiation. The inset shows the maximum decrement in π - π * absorbance within 5 s exposure time.

1182 (CN stretch), 1464 (NN stretch), 1487 (NN stretch), and 1600 cm⁻¹ (CC stretch) were characteristic vibrations of *trans* azobenzene, thus indicating that compound **1** was a thermodynamically stable *trans* product. Moreover, the absence of the in-plane ring bending mode at approximately 1440 cm⁻¹ might indicate the rigidity of azo compound **1** based on the fluorene framework.

Compared with *trans* aromatic azo compounds that have an intense π - π * absorption in the UV region, *trans* compound 1 (Figure 1b), with bilateral

electron-donating DPAF moieties, showed a broad and intense absorption band in the visible region centered at approximately 470 nm (with a molar extinction coefficient of ε at approximately $4.5 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$). This redshifted band, with a coplanar *trans* configuration, suggested that compound **1** had an elongating π -conjugation length and a lower bandgap energy of π - π * transition. Therefore, *trans*-to-*cis* photoisomerization for azo compound **1** was expected to transpire under the excitation of visible light instead of UV

Chem. Asian J. 2014, 9, 3390-3396

light. A first attempt that involved using a 467 nm argon ion laser (approximately 30 mW) as the excitation source could not produce any change in π - π * absorbance, thus indicating that compound 1 remained in the all-trans state. For performing the trans-to-cis photoisomerization, a higher radiant flux and a larger incident beam exposure area were introduced by employing a noncoherent light-emitting diode (LED) with a higher output energy (approximately 10 W) and a maximum blue emission of 466 nm. As shown in Figure 1b, on LED irradiation, absorbance at 470 nm rapidly reduced within several seconds and remained at a constant value for a longer exposure time. This partial decrease in absorbance was apparently due to the formation of a cis product with a relatively poor π -conjugation system and blueshifted π - π * absorption. The light-induced isomerization for a dilute solution of aromatic azo compounds generally results in either an all-trans or an all-cis photostationary state (PSS). However, the PSS for compound 1, established through blue LED irradiation and readily visualized using normal-phase TLC analysis, was composed of both trans and cis products. The $R_{\rm f}$ value of the cis isomer (0.55) was lower than that of the *trans* isomer (0.83), consistent with the fact that cis isomers possess a significant dipole moment and higher polarity. On the assumption that cis 1 would be completely transparent at 470 nm, cis content was calculated on the basis of a drop in blue-light absorbance of approximately 45% during LED irradiation; the trans isomer was the component in slight excess in this isomeric mixture.

In addition to a decrease in $\pi - \pi^*$ absorbance, we observed an increasing absorption band in the UV region of 350-400 nm. We speculated that this increasing band corresponded to the π - π * absorption of the *cis* isomer. Because the 2-amino-substituted DPAF precursor possessed intense UV absorption centered at 330 nm (with a molar extinction coefficient of ε at approximately $2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and because the *cis* isomer possessed a poor π conjugation on the central N=N bond, the cis isomer was expected to have a blue-shifted π - π * absorption band in the UV region. As indicated by this UV absorption band, the cis isomer could be switched back to the trans form with a 365 nm LED light. As shown in Figure 2a, the absorbance returned to its initial UV irradiation values within several seconds, and the trans/cis isomerization in solutions in both toluene and THF could be reversibly switched by alternating UV and bluelight irradiation. The photoisomerization of compound 1 manifested a notable difference from conventional azobenzene systems in that it possessed a reverse direction of the photoswitching wavelengths: a trans-to-cis interconversion with visible (blue) light but a cis-to-trans back-isomerization with UV light.

One- and two-dimensional ¹H NMR spectra of compound **1** (approximately 10^{-2} M in CDCl₃) from alternating visible and UV-light irradiation were compared (see the Supporting Information). Figure 2b shows the partial spectrum for symmetric all-*trans* **1** and the marked aromatic resonances, with H¹ and H² denoting the *ortho* protons adjacent to the N=N bond. The complexity of the aromatic protons after blue-



Figure 2. a) Reversible photoswitch for azo compound **1** upon alternating blue- and UV-light irradiation. ¹H NMR spectroscopic analysis for b) all*trans* **1**, and c) *trans/cis*-isomeric mixture by blue-light irradiation for 10 min. H¹ and H² denote the characteristic *ortho* protons adjacent to the N=N bond of *trans* isomer; H^3-H^7 denote the aromatic protons of *cis* isomer.

light irradiation, which ranged from $\delta = 6.9$ to 7.3 ppm, indicated the existence of both trans and cis products (Figure 2c). The distinguishable peaks of H^3 to H^7 denoted the characteristic protons on the cis structure. The integral area of the spectrum from H⁷ to either H¹ or H² gradually increased as the light exposure time was extended, thereby suggesting that the cis content in the isomeric mixture could be increased with a longer irradiation time. On the basis of the integral ratios between the typical protons of these two isomers, the calculated maximum *cis* content was approximately 30-40% under NMR spectroscopic experimental conditions. Moreover, after UV-light irradiation, all of the cis isomers were switched back to the trans form; thus, the obtained NMR spectrum was identical to the original spectrum of all-trans 1. NMR spectroscopic and UV/Vis absorption analyses confirmed an efficient and reversible trans/cis photoswitching of this fluorene-based azo compound in concentrated and dilute solutions, respectively.

The PSS for compound **1**, established through blue-light irradiation, contained both *trans* and *cis* isomers at a fixed ratio; further irradiation did not increase the *cis* content. The approach of the PSS is attributed to equal reaction rates of forward (*trans*-to-*cis*) and backward (*cis*-to-*trans*) in-

terconversions under 466 nm LED excitation. We assumed that the incomplete transformation was due to an increase in the backward reaction rate during light exposure and was dominated by two main factors. The first factor was the rapid thermal relaxation of the cis isomer to the thermodynamic trans product. Following the first-order kinetic shown in the Supporting Information, the thermal isomerization rate (k_t) calculated according to the recovery of $\pi - \pi^*$ absorbance at room temperature was determined to be $1.13 \times$ 10⁻² min⁻¹, approximately 20-fold faster than common azobenzenes, such as 4-butyl-4'-methoxyazobenzene (5.80× 10⁻⁴ min⁻¹).^[11] The more likely cause for the increasing backward thermal isomerization of cis 1 was the destabilization of the N=N bond by the bilateral electron-donating DPAF moieties.^[12] Secondly, the *cis* isomer might have undergone a symmetry-allowed $n-\pi^*$ transition in the visible region to cause the π - π * and n- π * transitions of *trans* and cis isomers, respectively, to possess similar energy gaps. Once the isomeric system contained certain amounts of cis isomers, blue-light irradiation induced the photoisomerization in both directions simultaneously. Thus, the equilibrium state was soon reached because of an accelerating backward reaction. We then employed high-performance liquid chromatography (HPLC) to separate the trans and cis isomers quickly and verify their UV/Vis absorption spectra through on-line photodiode array (PDA) detection. The HPLC chromatograms revealed two well-resolved peaks, the trans product at 2.9 min and the *cis* product at 3.1 min (Figure 3a). The increase in the integral ratio of cis/trans peaks under different light exposure times also confirmed that the cis content gradually increased until the PSS was reached. The absorption profile of trans 1 obtained from PDA detection in Figure 3b agreed with the UV/Vis spectrum shown in Figure 1b. Two distinct absorption bands for cis 1 were noticed in the UV and visible regions, which presumably corresponded to the π - π * and n- π * electronic transitions, respectively. Because of the overlap of the π - π * and n- π * absorption for trans and cis isomers, respectively, backward cis-totrans photoisomerization was also promoted under bluelight excitation. On the basis of the same molar extinction coefficients of trans and cis 1 at 300 nm (Figure 3b), the calculation of the integral areas for the two isomers from the chromatograms at this detection wavelength suggested a maximum cis content of 35%.

The irradiation time course of the *cis* contents was also established by using NMR spectroscopy to obtain the rate constant of k_p at PSS with a blue-light exposure. The experimental data fit the rate law well and yield the values of *cis* content (at PSS)=36.3% and $k_p=2.04\times10^{-1}$ min⁻¹ (Figure 3c).^[8b] Considering that k_p is the sum of the forward (k_f) and backward (k_b) reaction rate constants, the two rate constants of $k_f=0.74\times10^{-1}$ min⁻¹ and $k_b=1.3\times10^{-1}$ min⁻¹ were obtained. Because k_b is composed of both thermal (k_t) and photoisomerization rate constants, the accelerating backward *cis*-to-*trans* reaction was mainly found to be dominated by the n- π^* absorption of the *cis* isomer in the blue-light region. The calculated *cis* content at the PSS (approximately



Figure 3. a) HPLC chromatograms for azo compound 1. The *cis* content gradually increases with blue-light irradiation. b) UV-visible absorption profiles for pure *trans* and *cis* 1 analyzed by HPLC equipped with an online photodiode array (PDA) detector. c) Time course of *trans*-to-*cis* photoisomerization. The *cis* content is determined by ¹H NMR spectroscopy, and the solid line is the nonlinear curve fitting integrated rate law. The calculated *cis* content at photostationary state (approximately 36%) is consistent with the experimental value (approximately 35%) obtained using HPLC analysis.

36%), determined from its fit with the nonlinear curve of the rate law, was consistent with the experimental values (approximately 35%) obtained using HPLC analysis.

Because of the efficient nonradiative relaxation process that involves *trans/cis* isomerization, the azo compound **1** was nonfluorescent. Therefore, we introduced an open-aperture fs Z-scan technique to examine its 2PA behavior.^[13] Femtosecond laser pulses were generated by a mode-locked

Chem. Asian J. 2014, 9, 3390-3396

Ti:sapphire laser with a near-infrared (NIR) wavelength of 800 nm, a pulse width of 150 fs, and a repetition rate of 82 MHz. Both the *trans*- and *cis*-1 were completely transparent at 700–900 nm (Figure 3b), thus suggesting an absence of linear optical absorption in the NIR region. During data collection, laser pulses with a beam waist of approximately 20 μ m were focused onto the azo solution in a quartz cuvette with a path length of 1 cm. The incident and transmitted laser powers were monitored as the cuvette moved along the Z direction, toward and away from the focus position. Figure 4a shows the experimental Z-scan curves of *trans* 1, which were created by changing the input intensity per laser pulse (I_0), with significant 2PA signatures based on



Figure 4. a) Open-aperture Z-scan traces of azo compound 1 (5×10^{-3} M in toluene) by changing the input intensity of the laser beam (40, 60, 80, 100, 120 mW) at $\lambda_{ex} = 800$ nm. b) The correlation of (1/T-1) versus I_0 [GW cm⁻²]; T and I_0 denote the normalized transmittance value at Z = 0 cm and incident energy per laser pulse, respectively. c) The contrast of the Z-scan curves between 1 (1×10^{-2} M in toluene) and DO3 (1×10^{-2} M in THF) under identical input laser intensity (120 mW).

the decrease in normalized transmittance (*T*) at Z=0. The linear dependence between the amplitude of transmittance change (1/T-1) and I_0 also confirms a nonlinear 2PA process (Figure 4b).^[14] Moreover, Figure 4c shows the contrast of *Z*-scan traces between *trans* **1** and Disperse Orange III (DO3), a commercially available NLO azobenzene chromophore (D– π –A type).^[8a,c] Based on the minor change in the transmittance for DO3 under identical I_0 , the 2PA response for *trans* **1** is considerably higher than that for common azo dyes.

Considering the equivocal statement that 2PA intensity is usually lower for azobenzene (Ph-N=N-Ph) than for stilbene (Ph-C=C-Ph) derivatives, combining azo and rigid fluorene with bilateral electron-donating groups did enhance the 2PA cross-section in the NIR wavelength.^[8a] Although there was no clear understanding at the time of this study about the connection between the remarkable 2PA response and azo linkage, our results showed that such a structural combination leads to highly active 2PA chromophores. Furthermore, as shown in Figure 5a, the computational modeling of the



Figure 5. Optimized isosurface plots of the a) HOMO and b) LUMO for *trans*-1 analogue with 9,9-diethyl substitution, energetically minimized at the density functional B3LYP/6-31G** level under vacuum.

trans-**1** analogue with 9,9-diethyl substitution by using the B3LYP hybrid functional and the 6-31G** basis set shows that the highest-occupied molecular orbital (HOMO) is mainly delocalized over the DPAFs. Meanwhile, the electronic cloud of the lowest-unoccupied molecular orbital (LUMO) is condensed mostly on the central moiety (Figure 5b). This preliminary calculation implies an ICT process from the peripheral diphenylamines (donor) to the central CNNC group (acceptor) through a fluorene π bridge. Moreover, we conjectured that the ICT for azo compound **1** is more favored because of the relatively higher electronegativity of the central nitrogen atoms.

We also analyzed the 2PA intensity of the isomeric mixture at PSS, which was established by blue-light irradiation (approximately 65% of *trans* and 35% of *cis* products).

Chem. Asian J. 2014, 9, 3390-3396

Prior to the Z-scan experiment, the azo solution was exposed to blue light until the PSS was reached, and was then excited in situ by using laser pulses to trace the transmittance change at the focal point. Nevertheless, the normalized change in transmittance at Z=0 for the isomeric mixture was nearly identical to that of the all-trans-1 solution (see the Supporting Information). This result implied that, for both solutions, the chemical composition at the laser focusing spot was in the all-trans state. This is presumably due to the extremely unstable cis structure during the Z-scan measurement. The rate constants of k_t for thermal cis-totrans back-isomerization substantially increased as the surrounding temperature increased (see the Supporting Information), which suggests that the *cis* isomer became quite unstable with elevating temperatures. Because significant topical heating by laser pulses in high repetition frequency could have induced rapid and complete cis-to-trans thermal isomerization, the influence on 2PA properties in the presence of the cis isomer could not be determined under experimental conditions. Consequently, the preliminary results suggested that the fs 2PA behavior for azo chromophore 1 is quite uniform, regardless of the molecular geometry. To minimize the laser-induced thermal effect, a 2PA experiment that adopted an fs pulse laser with low repetition rate of 1 kHz as an excitation source is now under investigation.

In summary, we successfully demonstrated efficient trans/ cis photoisomerization and a significant third-order NLO response for the azo chromophore, simply incorporated with bilateral DPAF as a π framework. Although strong electrondonating DPAF moieties could destabilize the central N=N bond, reversibly switching the molecular geometry was still possible through non-coherent LED-light excitation at two wavelengths (466 and 365 nm). The PSS established by using blue light at room temperature was composed of only 36% cis isomer. This percentage was mainly due to an increasing cis-to-trans back-isomerization rate through both photo- (n- π^* absorption of *cis* isomer) and thermal isomerization routes. Compared with common azobenzene dyes, the fs Zscan measurement determined a significant enhancement of the 2PA intensity for this azo chromophore in its all-trans state. Because of extremely fast cis-to-trans thermal isomerization under accumulated and substantial heat generated by fs laser pulses, the influence on 2PA properties in the presence of the cis isomer was negligible at this stage. Based on different π -conjugation domains, we suggest that the *trans* and cis isomers exhibit distinct 2PA behaviors. A thermally stable cis-azo chromophore is necessary to achieve a tunable NLO response with respect to a change in molecular geometry.^[11] A study along this line is currently underway, and the findings will be reported in due course.

Experimental Section

Synthesis of Azo Compound 1

101 mg, 0.196 mmol) in toluene (2 mL) was purged with air for 5 min, and then stirred vigorously at 60 °C under air balloon for 20 h. After cooling to room temperature and being concentrated under vacuum, the residue was purified by silica flash column chromatography using a *n*-hexane and ethyl acetate mixture (19:1) as eluent to afford an orange solid of **1** (83.8 mg, 83%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.90 (d, *J* = 1.7 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 1.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 8H), 7.03 (t, *J* = 7.3 Hz, 6H), 2.05–1.96 (m, 4H), 1.92–1.85 (m, 4H), 1.18–1.00 (m, 24 H), 0.79 (t, *J* = 7.1 Hz, 12H), 0.69 ppm (m, 8H); ¹³C NMR (CDCl₃, 100 MHz): δ = 153.5, 152.1, 151.9, 148.1, 144.0, 135.5, 129.5, 124.3, 123.5, 123.1, 123.0, 121.3, 119.6, 119.1, 117.1, 55.5, 40.6, 31.8, 30.0, 24.1, 22.8, 14.3 ppm; MALDI-TOF-MS: *m*/z calcd for C₇₄H₈₅N₄ [*M*+H]⁺: 1029.68; found: 1029.81.

Acknowledgements

The authors would like to thank the Ministry of Science and Technology of Taiwan (MOST102-2113M-040-004) for financially supporting this research. The authors are also grateful to Prof. Toyoko Imae for support with micro-Raman measurements and to Prof. Ming-Yu Kuo for support with the computational modeling.

Keywords: absorption \cdot azo compounds \cdot charge transfer \cdot chromophores \cdot isomerization

- a) Y. Zhao, T. Ikeda in Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals, Wiley, New Jersey, 2009; b) R. Deloncle, A.-M. Caminade, J. Photochem. Photobiol. C 2010, 11, 25–45; c) M. Han, T. Honda, D. Ishokawa, E. Ito, M. Hara, Y. Norikane, J. Mater. Chem. 2011, 21, 4696–4702; d) S. Samanta, A. A. Beharry, O. Sadovski, T. M. McCormick, A. Babalhavaeji, V. Tropepe, G. A. Woolley, J. Am. Chem. Soc. 2013, 135, 9777–9784; e) S.-L. Chen, C.-C. Chu, V. K. S. Hsiao, J. Mater. Chem. C 2013, 1, 3529–3531.
- [2] N. Tamai, H. Miyasaka, Chem. Rev. 2000, 100, 1875-1890.
- [3] a) Y. Norikane, N. Tamaoki, Org. Lett. 2004, 6, 2595–2598; b) K. G. Yager, C. J. Barrett, J. Photochem. Photobiol. A 2006, 182, 250–261;
 c) D. P. Ferris, Y.-L. Zhao, N. M. Khashab, H. A. Khatib, J. F. Stoddart, J. I. Zink, J. Am. Chem. Soc. 2009, 131, 1686–1688; d) S. K. M. Nalluri, J. Voskuhl, J. B. Bultema, E. J. Boekema, B. J. Ravoo, Angew. Chem. Int. Ed. 2011, 50, 9747–9751; Angew. Chem. 2011, 123, 9921–9925; e) I. Tochitsky, A. Polosukhina, V. E. Degtyar, N. Gallerani, C. M. Smith, A. Friedman, R. N. Van Gelder, D. Trauner, D. Kaufer, R. H. Kramer, Neuron 2014, 81, 800–813.
- [4] J. A. Delaire, K. Nakatani, Chem. Rev. 2000, 100, 1817-1845.
- [5] Z. Sekkat, P. Prêtre, A. Knoesen, W. Volksen, V. Y. Lee, R. D. Miller, J. Wood, W. Knoll, J. Opt. Soc. Am. B 1998, 15, 401–413.
- [6] a) G. S. He, L.-S. Tang, Q. Zheng, P. N. Prasad, *Chem. Rev.* 2008, 108, 1245–1330; b) R. Rumi, S. Barlow, J. Wang, J. W. Perry, S. R. Marder, *Adv. Polym. Sci.* 2008, 213, 1–95; c) H. Xia, W.-Y. Zhang, F.-F. Wang, D. Wu, X.-W. Liu, L. Chen, Q.-D. Chen, Y.-G. Ma, H.-B. Sun, *Appl. Phys. Lett.* 2009, 95, 083118; d) S. Yao, K. D. Belfield, *Eur. J. Org. Chem.* 2012, 3199–3217; e) H. Wang, F. Jin, S. Chen, X.-Z. Dong, Y.-L. Zhang, W.-Q. Chen, Z.-S. Zhao, X.-M. Duan, *J. Appl. Polym. Sci.* 2013, 130, 2947–2956.
- [7] a) M. Albota, D. Beljonne, J. L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* 1998, 281, 1653–1656; b) K. D. Belfield, Y. Liu, R. A. Negres, M. Fan, G. Pan, D. J. Hagan, F. E. Hernandez, *Chem. Mater.* 2002, 14, 3663–3667; c) S. Yao, H.-Y. Ahn, X. Wang, J. Fu, E. W. V. Stryland, D. J. Hagan, K. D. Belfield, *J. Org. Chem.* 2010, 75, 3965–3974; d) T.-C. Lin, M.-H. Li, C.-Y. Liu, J.-H.

A mixture that contained CuBr (4.6 mg, 32.1μ mol), pyridine (10 μ L, 0.124 mmol), and 2-amino-substituted diphenylaminofluorene (DPAF,

Lin, Y.-K. Shen, Y.-H. Lee, *J. Mater. Chem. C* 2013, *1*, 2764–2772; e) T.-C. Lin, C.-Y. Liu, B.-R. Huang, J.-H. Lin, Y.-K. Shen, C.-Y. Wu, *Eur. J. Org. Chem.* 2013, 498–508.

- [8] a) L. Antonov, K. Kamada, K. Ohta, F. S. Kamounah, *Phys. Chem. Chem. Phys.* 2003, 5, 1193–1197; b) S. W. Magennis, F. S. Mackay, A. C. Jones, K. M. Tait, P. J. Sadler, *Chem. Mater.* 2005, *17*, 2059–2062; c) L. De Boni, L. Misoguti, S. C. Zilio, C. R. Mendonca, *ChemPhysChem* 2005, *6*, 1121–1125; d) T. V. Truong, C.-Y. Chen, N. V. Tabiryan, Y. R. Shen, *J. Opt. Soc. Am. B* 2007, *24*, 2623–2626; e) L. D. Boni, A. A. Andrade, S. B. Yamaki, L. Misoguti, S. C. Zilio, T. D. Z. Atvars, C. R. Mendonca, *Chem. Phys. Lett.* 2008, *463*, 360–363.
- [9] C. Zhang, N. Jiao, Angew. Chem. Int. Ed. 2010, 49, 6174–6177; Angew. Chem. 2010, 122, 6310–6313.
- [10] a) C.-M. Stuart, R. R. Frontiera, R. A. Mathies, J. Phys. Chem. A 2007, 111, 12072–12080; b) Y. B. Zheng, J. L. Payton, C.-H. Chung, R. Liu, S. Cheunkar, B. K. Pathem, Y. Yang, L. Jensen, P. S. Weiss, Nano Lett. 2011, 11, 3447–3452.

- [11] B.-K. Tsai, C.-H. Chen, C.-H. Hung, V. K. S. Hsiao, C.-C. Chu, J. Mater. Chem. 2012, 22, 20874–20877.
- [12] L. Li, F. He, X. Wang, N. Ma, L. Li, ACS Appl. Mater. Interfaces 2012, 4, 4927–4933.
- [13] a) J.-H. Lin, Y.-J. Chen, H.-Y. Lin, W.-F. Hsieh, J. Appl. Phys. 2005, 97, 033526; b) Y.-P. Chan, J.-H. Lin, C.-C. Hsu, W.-F. Hsieh, Opt. Express 2008, 16, 19900–19908; c) M. Wang, V. Nalla, S. Jeon, V. Mamidala, W. Ji, L.-S. Tan, T. Cooper, L. Y. Chiang, J. Phys. Chem. C 2011, 115, 18552–18559.
- [14] a) A. A. Said, M. Sheik-Bahae, D. J. Hagan, T. H. Wei, J. Wang, J. Young, E. W. V. Stryland, *J. Opt. Soc. Am. B* 1992, *9*, 405–414;
 b) W. J. Yang, D. Y. Kim, C. H. Kim, M.-Y. Jeong, S. K. Lee, S.-J. Jeon, B. R. Cho, *Org. Lett.* 2004, *6*, 1389–1392; c) K. D. Belfield, M. V. Bondar, F. E. Hernandez, O. V. Przhonska, S. Yao, *J. Phys. Chem. B* 2007, *111*, 12723–12729.

Received: July 29, 2014 Published online: October 7, 2014