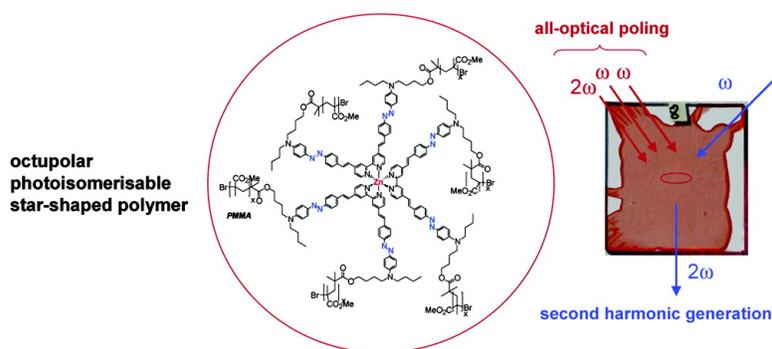Communication

All-Optical Orientation of Photoisomerizable Octupolar Zinc(II) Complexes in Polymer Films

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All-Optical Orientation of Photoisomerizable Octupolar Zinc(II) Complexes in Polymer Films

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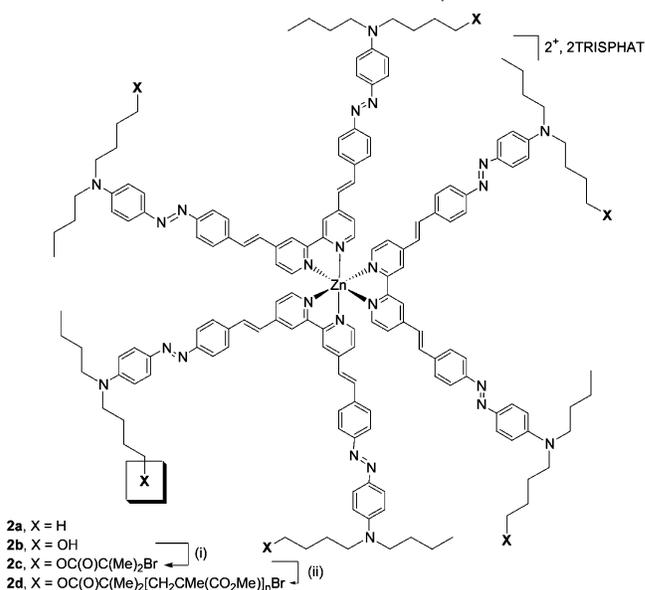
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The incorporation and noncentrosymmetric arrangement of NLO-phores into a macroscopic environment constitutes a key step toward the engineering of nonlinear materials and devices. In this regard, several strategies using *dipolar chromophores* have been intensively investigated, such as statistical orientation by electrical poling of NLO-polymers, stepwise construction of multilayers, supramolecular solid-state assemblies, or preorganization of NLO active species within multichromophoric systems.[1] By contrast, construction of macroscopic assemblies featuring octupolar chromophores remains in its infancy. A few examples of acentric organization of octupolar molecules by means of crystal engineering have been reported.[2,3] Because the traditional electric-field poling is not applicable due to the absence of permanent dipole moment, the so-called "all optical poling" technique has to be used to induce noncentrosymmetric ordering of multipolar molecules in polymer films.[4] This alternative procedure is based on a photoinduced angular hole-burning a*nd c*ombines two molecular excitation pathways, respectively excited at ω and 2ω (writing fields), followed by relaxation pathways involving mechanical reorientations such as photoisomerization. This technique is the only one capable of achieving the orientation of octupolar chromophores[4a] using appropriate writing polarizations.[4b] To obtain an optimum octupolar macroscopic order, the NLO-polymers must contain octupolar chromophores combining large molecular hyperpolarizability and photoisomerizable groups. Moreover, since the photoinduced orientation is in competition with Brownian motion in the polymer, grafting the molecule to the polymer chain is necessary to obtain a stable noncentrosymmetric order.[4c]

Previously, we described the use of 4,4′-bis(dialkylaminostyryl)-2,2′-bipyridines for the molecular engineering of octupolar D_3 metal-(II) complexes[5] and for the access to new star-shaped metallopolymeric NLO-phores.[6] With the aim of carrying out the optical orientation experiment, we have designed a new type of 4,4′-bis-(styryl)-2,2′-bipyridine functionalized by a dialkylamino-azobenzene group. This ligand allowed us to prepare photoisomerizable octupolar tris(bipyridyl)zinc(II) complexes and the corresponding star-shaped polymer by atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). Herein we report the photoisomerization properties of such new metallochromophores and present for the first time the macroscopic molecular orientation of the corresponding doped and star-shaped NLO-polymer films.

The target bipyridines **1a** and **1b** (Figure S1-Supporting Information) were readily prepared by means of a double Wadsworth–Emmons condensation between the "bisphosphonate-bipyridine"

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Scheme 1. Chemical Structures of Zinc Complexes **2a**−**d**[a]

2a, X = H
2b, X = OH
2c, X = OC(O)C(Me)₂Br ← (i)
2d, X = OC(O)C(Me)₂[CH₂CMe(CO₂Me)]ₙBr ← (ii)

a Conditions: (i) BrC(Me)₂C(O)Br, pyridine, THF, rt, 77%; (ii) MMA/CuBr/ *i*PrN=C−Py, (600/6/12), MeOH, 60 °C, 85%.

and the corresponding conjugated aldehydes. The corresponding tris(bipyridyl)zinc(II) complexes **2a,b** (Scheme 1) were classically prepared upon treatment of Zn(OAc)₂·2H₂O with three equivalents of ligands **1a,b** in refluxing ethanol, followed by metathesis with the TRISPHAT anion.[7] The metallo-initiator **2c** was further obtained by esterification of **2b** by means of 2-bromoisobutyroylbromide (Scheme 1 (i)). As previously described on model complexes,[6] ATRP of MMA was carried out in MeOH at 60 °C using a 600/6/12/1 ratio of MMA/CuBr/propyl-2-pyridylmethanimine/metallo-initiator (Scheme 1 (ii)). The resulting polymer **2d** (M_n = 63000, M_w = 68000, PDI = 1.07, T_g = 125 °C) contains ca. 8 wt % of metallochromophore. Two types of thin films were prepared by spin-coating on glass substrate from a trichloroethane solution containing either a commercial polycarbonate (T_g = 150 °C) doped by **2a** (**F₁**), or the grafted polymer **2d** (**F₂**). Scanning electron microscopy showed that both bulk materials present a very homogeneous aspect, a good optical quality, and a thickness of about 1 μm.

Bipyridines **1a,b** as well as the corresponding complexes **2a,b** exhibit a broad, intense intraligand charge transfer (ILCT) transition in the visible range at 480 and 496 nm respectively. The complexation is accompanied by a slight bathochromic shift of the ILCT band ($\Delta\lambda$ = 16 nm) but with a 3-fold enhancement of the oscillator strength.[5] As usually observed,[6] polymer **2d** displays in solution

Table 1. Optical Properties of Molecules and Materials

	λ_{max} (nm)	ϵ ($L \cdot mol^{-1} \cdot cm^{-1}$)	Φ_P (%)	K (s^{-1})
1a	480^a	76500	53^b	5.6×10^{-3}
2a	496^a	246000	28^b	1.25
F₁ (doped)	498	—	—	$2.8 \times 10^{-2}/4 \times 10^{-5}$
F₂ (star-shaped)	488^c	—	—	$0.78/3.7 \times 10^{-3}$

^{a} In CH_2Cl_2 solution. ^{b} In $CHCl_3$ solution. ^{c} λ_{max} of **2d** in CH_2Cl_2: 483 nm
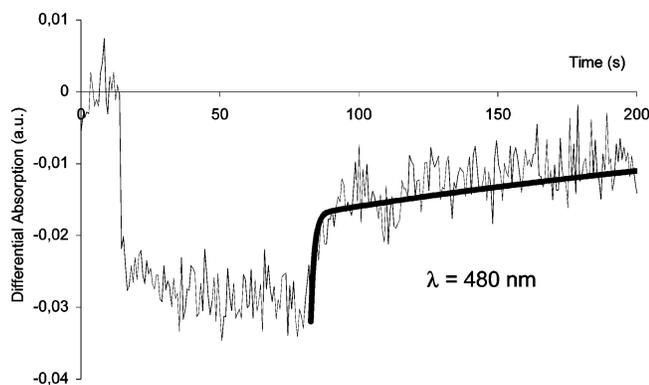

Figure 1. Kinetic study of the trans−cis−trans isomerization and corresponding simulation for the thermal relaxation (bold line) at 480-nm wavelength for the film **F2**.
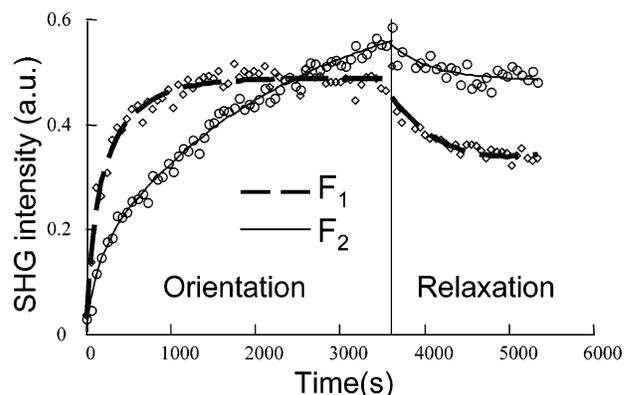

Figure 2. Optical orientation and relaxation of **F₁** and **F₂** under resonant one- and two-photon excitations (open circles and diamonds) compared to a biexponential plot (lines).

or in thin film (**F₂**) absorption spectra very similar to those of **2a**, indicating that the structure is conserved upon polymerization (Table 1). Harmonic light-scattering measurements, performed in CH_2Cl_2 solution using 1.91 μm as fundamental wavelength, revealed that **2a** exhibits an exceptional NLO activity with a β value of 863×10^{-30} esu ($\beta_0 = 590 \times 10^{-30}$ esu).

The photoisomerization properties of ligand **1a** and complex **2a** were studied in chloroform solution. For the complexes, the corresponding polymer films **F₁** and **F₂** were also studied. All samples show the usual behavior of azobenzene derivatives:[8] an important decrease of the main absorption $\pi-\pi*$ band in the 480−500-nm region and an increase of absorption around 370 nm (Figure 1). The minimum conversion extent Φ_p was determined by measuring the decrease of the absorption at λ_{max}, assuming that the cis isomer does not absorb at this wavelength. Thermal cis−trans reaction rate constants were determined by fitting the absorbance change in the dark of previously irradiated samples at 480 nm. As expected, **1a** and **2a** exhibit an exponential law (Figure S2-Supporting Information). The rate constant for **1a** is in the usual range for such substituted azobenzenes.[8b] Surprisingly, the thermal cis−trans reaction rate of **2a** is more than 2 orders of magnitude higher than for the corresponding ligand. In polymer films, the thermal cis−trans reaction was fitted by a biexponential law, which is characteristic of the existence of different free volumes around the chromophores.[9]

The optical noncentrosymmetric orientation of the octupolar molecules was performed on polymeric thin films **F₁** and **F₂**, and the dynamic behavior of the doped film **F₁** is compared to that of the star-shaped polymer **F₂**. The poling fundamental and harmonic frequencies are 1.064 μm and 532 nm, respectively. Both samples have an equal optical density of 0.165 at 532 nm which ensures equivalent one- and two-photon absorptions. A copropagating experimental configuration was implemented for the one- and two-photon excitation processes with parallel linear polarizations.[4d] The orientation dynamics were followed by measuring, every 60 s, the second harmonic generated (SHG) by the poled sample using the 1.064-μm field and are given in Figure 2 for **F₁** and **F₂**. The

orientation process is stopped after 1 h, and the relaxation of the SHG signal is followed during 30 min. The dynamics, which are plotted using a biexponential function, show a slower but more efficient orientation of the star-shaped polymeric film. After reaching a stationary state, **F₂** exhibits a 40% higher SHG intensity than **F₁** (extrapolated from the exponential plots), whereas the relaxation induces a loss of 25% of the induced SHG intensity for **F₁** and only 10% for **F₂**. This demonstrates that grafting the octupolar chromophores has allowed the molecular reorientation processes to dominate more efficiently the molecular Brownian motion, therefore inducing a higher and more stable photoinduced noncentrosymmetry.

In summary, this work provides the first example of all-optical poling orientation of a photoisomerizable star-shaped NLO-polymer. This result shows the possibility to generate a new class of nonlinear quadratic materials, capable of answering the request of stability and efficiency in conjunction with the symmetry control.

Supporting Information Available: Synthetic procedures, complete characterizations, Figures S1 and S2, and experimental setups. This material is available free of charge via the Internet at http://pub.acs.org.

References

(1) (a) Burland, D. M. *Chem. Rev.* (special issue) **1994**, *94*, 1−278. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155−173. (c) van der Boom, M. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3363−3366.
(2) (a) Cho, B. R.; Lee, S. J.; Lee, S. H.; Son, K. H.; Kim, Y. H.; Doo, J.-Y.; Lee, G. J.; Kang, T. I.; Lee, Y. K.; Cho, M.; Jeon, S.-J. *Chem. Mater.* **2001**, *13*, 1438−1440. (b) Evans, O.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511−522. (c) Zyss, J.; Ledoux-Rak, I.; Weiss, H.-C.; Bläser, D.; Boese, R.; Thallapally, P. K.; Thalladi, V. R.; Desiraju, G. R. *Chem. Mater.* **2003**, *15*, 3063−3073.
(3) For a supramolecular organization of octupoles see: Le Bouder, T.; Maury, O.; Bondon, A.; Costuas, K.; Amouyal, E.; Ledoux, I.; Zyss, J.; Le Bozec, H. *J. Am. Chem. Soc.* **2003**, *125*, 12284−12299.
(4) (a) Fiorini C.; Nunzi, J.-M.; Raimond, P.; Branger, C.; Lequan, R. M. *Synth. Met.* **2000**, *115*, 127−131. (b) Brasselet, S.; Zyss, J. *Opt. Lett.* **1997**, *22*, 1464−1466. (c) Fiorini; Nunzi, J.-M. *Chem. Phys. Lett.*, **1998**, *286*, 415−420. (d) Brasselet, S.; Bidault, S.; Zyss, J. *C. R. Phys.* **2002**, *3*, 479−492.
(5) Sénéchal, K.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **2002**, *124*, 4561−4562.
(6) Viau, L.; Even, M.; Maury, O.; Haddleton, D. M.; Le Bozec, H. *Macromol. Rapid Commun.* **2003**, *24*, 630−635.
(7) Lacour, J.; Glinglinger, C.; Grivet, C.; Bernardelli,G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 608.
(8) (a) Rau, H. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Raton, FL, 1990; pp 119−141 and references therein. (b) Rau, H. In *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp 165−192 and references therein.
(9) (a) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171−177. (b) Böhm, N.; Materny, A.; Kiefer, W.; Steins, H.; Müller, M. M.; Schottner, G *Macromolecules* **1996**, *29*, 2599−2604.