

Efficient Modulation of the Third Order Nonlinear Optical Properties of Fullerene Derivatives

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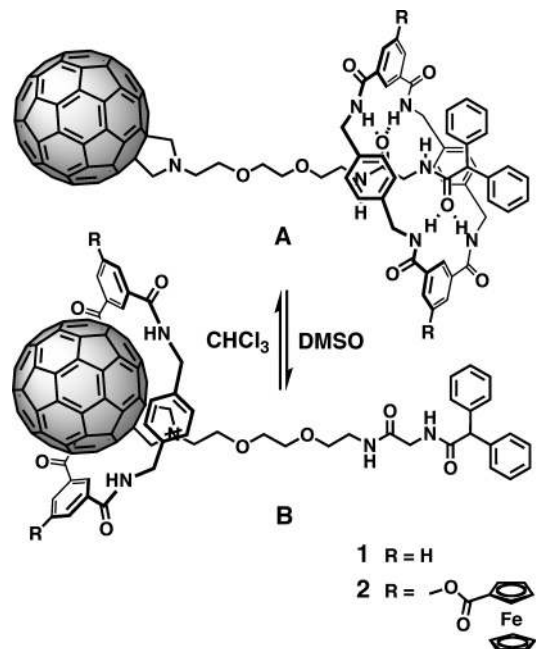
Molecular machines^{1,2} are devices that can perform precise tasks derived from the motion of their different submolecular components. Typical examples of such molecular machines, known as rotaxanes, display an analogous structure to that of an abacus. During the last years, bistable rotaxanes (“molecular shuttles”) have been the subject of several investigations as they are considered promising candidates for potential applications in optoelectronics.^{3–5} These include optical switching operations at the molecular level, given that the wheel component (macrocycle) can be reversibly positioned in different parts of the thread under controlled conditions. Indeed, shuttling has been demonstrated to be a useful tool for modifying macroscopic properties at the molecular level. Recently, some examples have been reported, in which molecular motion has been intentionally applied to modulate physicochemical properties with potential applicability in technology, including fluorescence,^{6–8} photoinduced electron transfer events,⁸ circular dichroism,⁹ chemical stability,¹⁰ and surface properties.^{11,12}

Fullerenes are known to exhibit a sizable nonlinear optical (NLO) response^{13,14} due to their large π -conjugated surface and the extensive charge delocalization.¹⁵ As molecular shuttles, fullerenes are of great interest for the development of materials for photonic applications.^{16–18} In this regard, C₆₀-based molecular shuttles¹⁹ are considered to be very promising candidates as photonic elements (e.g., optical switches and deflectors) not only because of the inherent properties of fullerenes but also because fullerenes have been shown to induce shuttling.^{7,8,19,20}

In the present work, we report for the first time how the submolecular rearrangement of the different counterparts of fullerene-stoppered molecular shuttles results in the modulation of the microscopic third order NLO response of fullerene derivatives, demonstrating their potential for optical applications. In fact, it was found that the co-conformations **A** and **B** of molecular shuttles **1** and **2** (Scheme 1) exhibit a substantial difference in their third order NLO response. It was also observed that the response of **2** is enhanced in comparison with **1** due to electron transfer between the ferrocene moieties present on the macrocycle and the fullerene.

Molecular shuttles **1**⁷ and **2**⁸ exist preferentially in two different co-conformations (Scheme 1). In CHCl₃, the macrocycle adopts primarily co-conformation **A** due to hydrogen bond interactions between the macrocycle and the peptidic station on the thread. On the other hand, in DMSO, the hydrogen bonds are weakened, which releases the macrocycle from the peptidic station, promoting the establishment of π – π interactions between the fullerene and the macrocycle. This results in the translocation of the macrocycle to

Scheme 1. Structure and Behavior of the Thread and the Molecular Shuttles



the opposite end of the thread, adopting preferentially the stacked co-conformation **B** (Scheme 1).

The NLO response of molecular shuttles **1** and **2** was measured by means of Z-scan technique,^{21,22} employing 35 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser. The NLO response of the solvents employed for the preparation of each co-conformer (i.e., CHCl₃ and DMSO) was measured and taken into account in order to obtain the nonlinearity of the solute. Different solutions of several concentrations of molecular shuttles **1** and **2** were prepared in CHCl₃ (co-conformation **A**) and in DMSO (co-conformation **B**), while their UV–vis spectra were regularly recorded before and after each measurement in order to check for any photoinduced effects and also to confirm that no degradation had occurred. The solutions of **1** and **2** were found to exhibit a positive lens behavior (i.e., focusing) corresponding to a positive sign nonlinearity (i.e., $\text{Re}\chi^{(3)} > 0$).

The real and imaginary parts of the third order susceptibility, $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$, of each molecular shuttles' solution were determined from the analysis of several Z-scan measurements performed for each different concentration varying the laser intensity, as reported elsewhere.^{13,17,21,22} Figure 1 exemplifies the variation of the $\text{Re}\chi^{(3)}$ values corresponding to co-conformer **1A** as a function of the concentration, in which a very good linear

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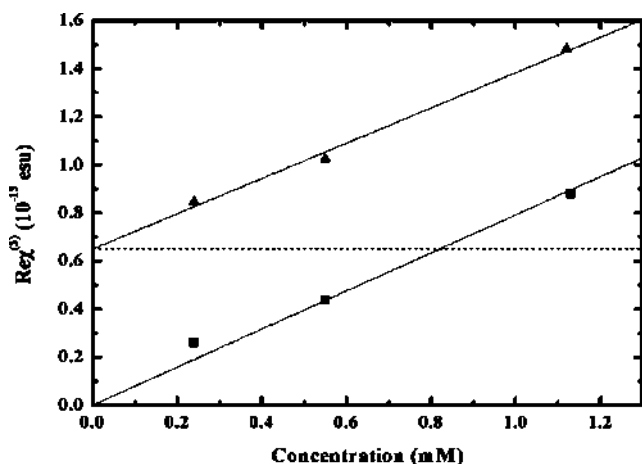


Figure 1. $\text{Re}\chi^{(3)}$ values as a function of the concentration. (▲) **1** in CHCl_3 (co-conformer **1A**); (•••) CHCl_3 ; (■) contribution of **1A**.

Table 1. NLO Response of the Different Co-conformers of Molecular Shuttles **1** and **2**

	$\text{Re}\gamma$ (10^{-32} esu)	γ (10^{-32} esu)
1A	4.09 ± 0.39	4.18 ± 0.48
1B	1.94 ± 0.64	2.19 ± 0.64
2A	5.40 ± 0.50	8.71 ± 0.62
2B	2.80 ± 0.20	4.80 ± 0.80

correlation holds (the solid line corresponding to the best linear fit). Each point of Figure 1 is derived from the intensity dependence of the $\Delta T_{\text{P-V}}$ parameter of each solution according to standard Z-scan procedures. Similar plots were constructed for the remaining co-conformations of shuttles **1** and **2**. Then, the real part of the second hyperpolarizability ($\text{Re}\gamma$) of each co-conformer was deduced from the slopes of the linear fits of these plots.

The obtained $\text{Re}\gamma$ and γ values are presented in Table 1. These values clearly show that shuttling rules the NLO response. As a matter of fact, the translocation of the macrocycle gives rise to a 2-fold difference of the NLO response when comparing co-conformers **A** and **B** of molecular shuttles **1** and **2**. A plausible explanation to this effect could be attributed to the existence of π - π interactions between the fullerene and the macrocycle in co-conformer **B** that are not entirely present in the case of co-conformer **A**. Indeed, such π - π interactions have already been shown to effect changes in other physical properties such as absorption, fluorescence, and the electrochemical potential.^{7,8,20} This is in strong agreement with the fact that the $\Delta\gamma_{\text{A-B}}$ is independent of the presence of the ferrocene units.

Moreover, molecular shuttle **2** was found to exhibit an overall 2-fold enhancement of γ when compared with **1**. This trend is consistent with previous work, in which an enhancement of the NLO response was observed as a result of efficient photoinduced electron transfer occurring from an electron donor (i.e., porphyrin, ferrocene) to C_{60} .²³ In effect, electron transfer between the ferrocene moieties and the fullerene of molecular shuttle **2** has been previously observed and described.⁸ Therefore, it can be affirmed that independently of shuttling, electron transfer dominates the general NLO expression.

We have demonstrated for the first time how submolecular motion, effected by π - π interactions, can be applied to manipulate the microscopic third order NLO response of fullerene derivatives.

Additionally, this response can be boosted when coupled with electron transfer events. This approach makes fullerene-based molecular shuttles very attractive candidates for photonic applications and opens the door to the design of novel light- and electrochemically switchable molecular shuttles, which ultimately could find application as photonic elements and thus the application of molecular machines in current technology. Current investigations will provide a better picture of the effects of shuttling in the NLO response, in which π - π interactions might influence the polarizability of the fullerene π -cloud, contributing directly to the NLO response.

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References

- (1) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.
- (2) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349–3391.
- (3) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391–394.
- (4) Jiang, L. S.; Okano, J.; Orita, A.; Otera, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2121–2124.
- (5) Flood, A. H.; Wong, E. W.; Stoddart, J. F. *Chem. Phys.* **2006**, *324*, 280–290.
- (6) Perez, E. M.; Dryden, D. T. F.; Leigh, D. A.; Teobaldi, G.; Zerbetto, F. *J. Am. Chem. Soc.* **2004**, *126*, 12210–12211.
- (7) Mateo-Alonso, A.; Fioravanti, G.; Marcaccio, M.; Paolucci, F.; Rahman, G. M. A.; Ehli, C.; Guldi, D. M.; Prato, M. *Chem. Commun.* **2007**, 1945–1947.
- (8) Mateo-Alonso, A.; Ehli, C.; Rahman, G. M. A.; Guldi, D. M.; Fioravanti, G.; Marcaccio, M.; Paolucci, F.; Prato, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3521–3525.
- (9) Bottari, G.; Leigh, D. A.; Perez, E. M. *J. Am. Chem. Soc.* **2003**, *125*, 13360–13361.
- (10) Mateo-Alonso, A.; Brough, P.; Prato, M. *Chem. Commun.* **2007**, 1412–1414.
- (11) Berna, J.; Leigh, D. A.; Lubomska, M.; Mendoza, S. M.; Perez, E. M.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Nat. Mater.* **2005**, *4*, 704–710.
- (12) Bunker, B. C.; Huber, D. L.; Kushmerick, J. G.; Dunbar, T.; Kelly, M.; Matzke, C.; Cao, J. G.; Jeppesen, J. O.; Perkins, J.; Flood, A. H.; Stoddart, J. F. *Langmuir* **2007**, *23*, 31–34.
- (13) Couris, S.; Koudoumas, E.; Ruth, A. A.; Leach, S. J. *Phys. B: At. Mol. Opt. Phys.* **1995**, *2*, 4537–4554.
- (14) Koudoumas, E.; Konstantaki, M.; Mavromanolakis, A.; Couris, S.; Fanti, M.; Zerbetto, F.; Kordatos, K.; Prato, M. *Chem.—Eur. J.* **2003**, *9*, 1529–1534.
- (15) Guldi, D. M. *Chem. Commun.* **2000**, 321–327.
- (16) Koudoumas, E.; Konstantaki, M.; Mavromanolakis, A.; Michaut, X.; Couris, S.; Leach, S. J. *Phys. B: At. Mol. Opt. Phys.* **2001**, *34*, 4983–4996.
- (17) Couris, S.; Koudoumas, E. Nonlinear Optical Properties of Fullerenic Materials. In *Nonlinear Optical Responses of Molecules, Solids and Liquids: Methods and Applications*; Papadopoulos, M. G., Ed.; Research Signpost: Trivandrum, India, 2003; p 231.
- (18) Signorini, R.; Bozio, R.; Prato, M. Optical Limiting Applications. In *Fullerenes: From Synthesis to Optoelectronic Properties*; Martin, N., Guldi, D. M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2002; p 295.
- (19) Mateo-Alonso, A.; Guldi, D. M.; Paolucci, F.; Prato, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8120–8126.
- (20) Mateo-Alonso, A.; Fioravanti, G.; Marcaccio, M.; Paolucci, F.; Jagesar, D. C.; Brouwer, A. M.; Prato, M. *Org. Lett.* **2006**, *8*, 5173–5176.
- (21) Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.
- (22) Couris, S.; Koudoumas, E.; Konstantaki, M. Characterization of Nonlinear Optical Materials for Photonic Applications. In *NATO Science Series 3: High Technology*; 2000; Vol. 75, p 143.
- (23) Xenogiannopoulou, E.; Medved, M.; Iliopoulos, K.; Couris, S.; Papadopoulos, M. G.; Bonifazi, D.; Soombar, C.; Mateo-Alonso, A.; Prato, M. *ChemPhysChem* **2007**, *8*, 1056–1064.

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