# The unexpected similar second-order NLO response for nearly planar and largely twisted push–pull stilbazole chromophores: EFISH and theoretical TD-DFT evidence

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**The molecular second-order nonlinear optical properties of planar (*E*)-4-[2-(4-(*N*-methyl-*N*-hexadecylaminophenyl)ethenyl]pyridine ($L^1$) and [*cis*-$Ir(CO)_2ClL^1$] and of the significantly twisted new chromophores (*E*)-4-[(5,6,7,8-tetrahydro-5-isoquinolylidene)methyl]-*N*-methyl-*N*-hexadecylaniline ($L^2$) and [*cis*-$Ir(CO)_2ClL^2$] are reported, evidencing for the first time that planarity of a conventional (donor)(π-bridge)(acceptor) structure is not compulsory to reach a large NLO response.**

Over the past 20 years a lot of work has been dedicated to the molecular design of 1D organic push–pull π systems with high second order nonlinear optical (NLO) properties, because of their potential applications in various fields including telecommunications, optical data storage and processing.[1] A fundamental investigation of the structure–property relationship has highlighted a dependence of the quadratic hyperpolarizability on conjugation planarity.[2] A decrease of π-electron overlap due to a non-planar geometry should hamper donor–acceptor communication and reduce thus the quadratic hyperpolarizability ($\beta$).[2] Following these assumptions it is traditionally thought that conjugation planarity is a pre-requisite to maximize quadratic hyperpolarizabilities. An exception is the case of dipolar zwitterionic molecules with twisted π-electron systems joining a donor and an acceptor group which are expected to exhibit very high $\beta$ values as suggested by recent theoretical investigations.[3] In this particular case, contrarily to conventional organic π-conjugated chromophores, the structural characteristic that promotes these peculiar optical features is a stereochemically enforced diminution in the conjugation that enforces zwitterionic behavior in the ground state and provides a strong intramolecular excitation feature of low energy and high oscillator strength.[3] Besides, it was recently reported that self-assembled monolayers with sterically hindered (donor)(π-bridge)(acceptor) moieties, in which the donor and acceptor are twisted out of plane, exhibit molecular rectification, whereas those that are planar do not.[4] Therefore the structural characteristics of a given (donor)(π-bridge)(acceptor) moiety may influence greatly its electronic and optical properties.

We have now found that the quadratic hyperpolarizability of a conventional planar chromophore such as (*E*)-4-[2-(4-(*N*-methyl-*N*-hexadecylamino)phenyl)ethenyl]pyridine ($L^1$, Fig. 1) and its complex [*cis*-$Ir(CO)_2ClL^1$] is similar to that of a structurally related, but significantly twisted, chromophore, (*E*)-4-[(5,6,7,8-tetrahydro-5-isoquinolylidene)methyl]-*N*-methyl-*N*-hexadecylaniline ($L^2$, Fig. 1) and its complex, [*cis*-$Ir(CO)_2ClL^2$], respectively, evidencing for the first time that in traditional 1D push–pull organic chromophores a planar structure is not a compulsory requirement for significant second-order NLO response.

We reported recently that the quadratic hyperpolarizability $\beta$ of [*cis*-$Ir(CO)_2ClL^1$], measured in solution by the electric-field induced second harmonic (EFISH) generation technique,[5] is high[6] (Table 1) and that the product $\mu\beta_0$ is comparable to that of important organic chromophores such as Disperse Red One.[7] In order to verify the effect of some torsion on the quadratic hyperpolarizability of $L^1$ and of its complex [*cis*-$Ir(CO)_2ClL^1$], the chromophore $L^2$ was obtained by demethylation of the related methylpyridinium salt[8,9] and consequently its complex [*cis*-$Ir(CO)_2ClL^2$].[10] The product $\mu\beta_{1.907}$ of $L^1$, $L^2$ and the related

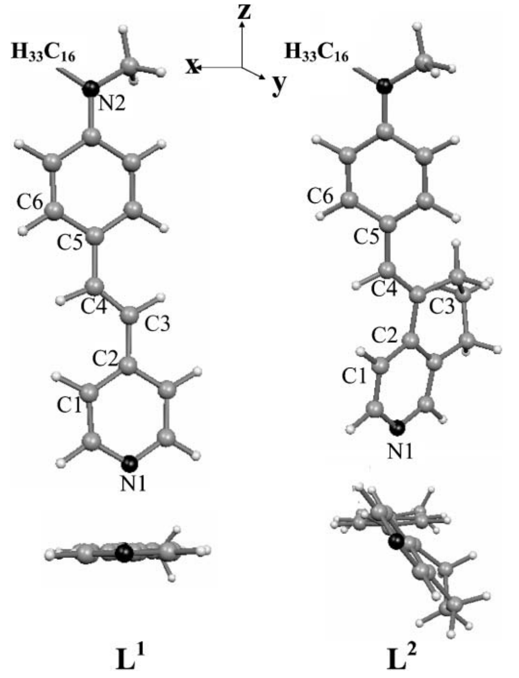

**Fig. 1** Optimized molecular structures of the $L^1$ and $L^2$ ligands. Black: N, gray: C, white = H atoms.

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**Table 1** Experimental electronic spectra ($\lambda_{max}$), dipole moments ($\mu$), EFISH quadratic hyperpolarizabilities at 1.907 μm (EFISH $\beta_{1.907}$) and product EFISH $\mu\beta_{1.907}$ in $CHCl_3$ for $L^1$ and $L^2$ ligands and related Ir(I) complexes

| Compound | $\lambda_{max}$/nm | $\mu^a$/D | EFISH $\mu\beta_{1.907}{}^b$/ $10^{-30}$ D cm$^5$ esu$^{-1}$ | EFISH $\beta_{1.907}$/ $10^{-30}$ cm$^5$ esu$^{-1}$ | Reference |
|---|---|---|---|---|---|
| $L^1$ | 381 | 4.0 | 220 | 55 | This work |
| *cis*-[Ir(CO)$_2$ClL$^1$] | 442 | 7.5 | 755 | 101 | 6 |
| $L^2$ | 369 | 5.0 | 235 | 47 | This work |
| *cis*-[Ir(CO)$_2$ClL$^2$] | 426 | 7.2 | 618 | 81 | This work |

[a] The error on $\mu$ is ± 0.5 D. [b] The error on EFISH measurements is ± 10%.

Ir(I) complexes were measured in $CHCl_3$ working with a non-resonant incident wavelength of 1.907 μm by the EFISH technique[5] whereas the dipole moments $\mu$ were measured in $CHCl_3$ according to the Guggenheim method.[11]

The absorption band at 381 and 442 nm (Table 1), attributed to the ILCT (intraligand charge transfer) n→ π* transition which dominates the second order nonlinear response,[12] of $L^1$ and [*cis*-Ir(CO)$_2$ClL$^1$], are 12 and 16 nm red shifted when compared to $L^2$ and [*cis*-Ir(CO)$_2$ClL$^2$], respectively, whereas both dipole moments and quadratic hyperpolarizability values are similar within the experimental error of the techniques. These remarkable results suggest that, in contrast to what is usually thought, a deviation from planarity does not influence significantly the second-order NLO response of this kind of conventional chromophore.

To gain insight into the structural, electronic and NLO properties of $L^1$ and $L^2$ we performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.[13] Main optimized geometrical parameters and calculated HOMO and LUMO energies, HOMO − LUMO gaps, absorption maxima, dipole moments ($\mu$), EFISH hyperpolarizabilities ($\beta$) and $\mu\beta$ products are reported in Table 2. The most noticeable difference between the structures of the two ligands is that a considerable twisted geometry is calculated for $L^2$, as opposed to the almost perfect planar geometry calculated for $L^1$. Thus, while for $L^1$ the two aromatic rings connected by the C3–C4 double bond are essentially coplanar (<C1–C2–C5–C6 = −1.3°) for $L^2$ the two rings form a dihedral angle of −56.1°, see Fig. 1. The other geometrical parameters are similar in the two chromophores, even though a general lengthening of the bond distances connecting the C2, C3 and C4 carbon atoms occurs in the structure of $L^2$, reflecting a partial disruption of π-conjugation introduced by the twisted structure (Table 2).

**Table 2** Calculated main geometrical parameters *in vacuo* (solution), HOMO and LUMO energies, HOMO − LUMO gaps, absorption maxima, dipole moments ($\mu$), EFISH quadratic hyperpolarizabilities at zero frequency ($\beta_0$), EFISH quadratic hyperpolarizabilities at 1.907 μm ($\beta_{1.907}$) and the product $\mu\beta_{1.907}$ for the $L^1$ and $L^2$ ligands

| Parameter | $L^1$ | $L^2$ |
|---|---|---|
| *d*(C1–C2)/Å | 1.406(1.408) | 1.407(1.408) |
| *d*(C2–C3)/Å | 1.461(1.460) | 1.483(1.483) |
| *d*(C3–C4)/Å | 1.348(1.351) | 1.354(1.356) |
| *d*(C4–C5)/Å | 1.456(1.455) | 1.464(1.463) |
| *d*(C5–C6)/Å | 1.405(1.407) | 1.406(1.409) |
| <C2–C3–C4/° | 126.5(126.2) | 120.7(120.6) |
| <C3–C4–C5/° | 127.8(127.7) | 129.7(130.0) |
| <C1–C2–C5–C6/° | −1.3(−5.0) | −56.1(−51.7) |
| HOMO/eV | −5.14 | −5.11 |
| LUMO/eV | −1.69 | −1.49 |
| Δ(HOMO − LUMO)/eV | 3.45 | 3.62 |
| Abs. Max./eV (data in nm in parenthesis) | 3.15 (393) | 3.24 (382) |
| $\mu$/D | 10.7 | 9.4 |
| $\beta_0/10^{-30}$ cm$^5$ esu$^{-1}$ | 21 | 19 |
| $\beta_{1.907}/10^{-30}$ cm$^5$ esu$^{-1}$ | 30 | 27 |
| $\mu\beta_{1.907}/10^{-30}$ D cm$^5$ esu$^{-1}$ | 321 | 254 |

The calculated electronic structure for the two chromophores reflects their different geometries. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are, respectively, π and π* combinations with a similar spatial arrangement for $L^1$ and $L^2$. The HOMO is mainly localized on the C3–C4 double bond and the aromatic moiety, while the LUMO is mainly localized on the C3–C4 double bond and on the pyridine moiety (see Fig. 2). The HOMO energies of $L^1$ and $L^2$ are quite similar (−5.14 and −5.11 eV, respectively) while the LUMO of $L^2$ is found to be destabilized by 0.20 eV with respect to that of $L^1$, see Table 2. Therefore, the increased HOMO − LUMO gap calculated for $L^2$ (3.62 *vs.* 3.45 eV for $L^1$) is essentially related to the LUMO destabilization in $L^2$. The calculated absorption maxima of $L^1$ and $L^2$ in $CHCl_3$ solution are originated by single HOMO − LUMO transitions at 3.15 eV (393 nm) and 3.24 eV (382 nm), respectively, in excellent agreement with experimental values of 381 and 369 nm. Bearing in mind the electronic structure picture discussed above, the small blue-shift observed for the absorption spectrum of $L^2$ with respect to that of $L^1$ appears thus to be related to the slight LUMO destabilization due to the twisting of the aromatic and pyridine rings.

Although larger than experimental values, dipole moments calculated in $CHCl_3$ solution for $L^1$ and $L^2$ are quite similar both at the B3LYP/6-311G* and BPW91/TZP (Table 2) levels (8.8 *vs.* 10.7 and 7.3 *vs.* 9.4 D, for $L^1$ and $L^2$, respectively). Despite an

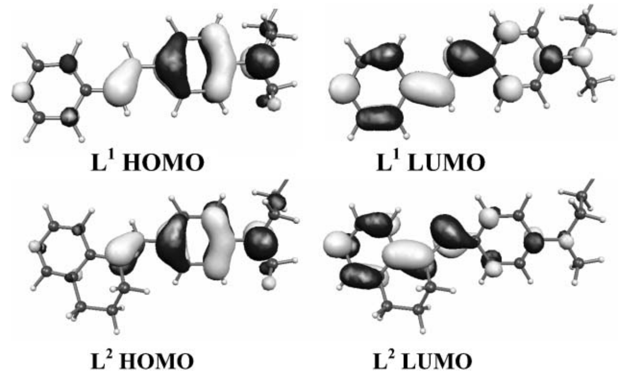

**Fig. 2** Isodensity surface plots of the HOMO and LUMO of the $L^1$ and $L^2$ ligands. Isodensity value 0.04. The alkyl chains have been omitted for clarity.

inversion with respect to the experimental trend, calculated values confirm the similarity of the dipole moments for the two ligands. Geometry optimization in solution at the B3LYP/6-311G* level, led to small changes in the geometrical parameters (Table 2) and dipole moments (9.0 *vs.* 8.8 and 8.1 *vs.* 7.3 D, for $L^1$ and $L^2$, respectively). In all the cases, the largest and dominating dipole moment component is the one aligned along the $z$ axis.

Static and frequency-dependent hyperpolarizabilities[20] calculated at the BPW91/TZP level in $CHCl_3$ solution, agree with experimental EFISH data ($\beta_{1.907}$ = 30 *vs.* 55 and 27 *vs.* 47 × $10^{-30}$ esu$^{-1}$ cm$^5$, for $L^1$ and $L^2$, respectively; see Tables 1 and 2) in order of magnitude. Similar to what was observed for the dipole moments, for both $L^1$ and $L^2$ the largest and dominating $\beta$ component is the *zzz* one. Our computational results are in line with previous theoretical calculations using Hartree–Fock and semi-empirical methods on the (*E*)-4-[2-(4-(*N,N*-dimethylamino)-phenyl)ethenyl]pyridine species, similar to $L^1$, showing larger (smaller) dipole moment (hyperpolarizability) values compared to experimental data in $CHCl_3$.[12,21] Most notably, calculated $\beta$ values, although smaller than experimental ones, confirm that the two ligands possess similar NLO responses, despite the marked differences in their geometrical structures. A rationale for this behavior possibly resides in the fact that the energies of the HOMO and LUMO of the two ligands, which are the orbitals involved in the transition dominating the NLO response, are not dramatically sensitive to the twisting of the double C–C bond, as confirmed by the similar experimental and calculated absorption maxima energies. This is due to the fact that the two orbitals have maximum amplitudes in the donor and acceptor moieties, with only a relatively small fraction being localized on the C–C double-bond, which is the unit most sensitive to the twisted geometry.

In conclusion, in contrast to what is traditionally thought, we produced both experimental and theoretical evidence that planarity of a conventional (donor)(π-bridge)(acceptor) structure *is not compulsory* to reach a large NLO response. Such an observation is of particular importance in the design of new chromophores for second-order nonlinear optics.

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10 Reaction of $L^2$ with $[Ir(CO)_2Cl]_2$ gave [*cis*-$Ir(CO)_2ClL^2$], as previously reported for similar ligands.[12] IR (in $CH_3CN$): $\nu$(CO) 2073 (s), 1993 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 0.87 (t, 3H, $J$ = 6.4 Hz, $CH_3$), 1.28 (m, 24 H, $CH_2$), 1.56 (m, 4H, $CH_2$), 1.87 (quintet, 2H, $J$ = 6.1 Hz, $CH_2$), 2.79 (t, 2H, $J$ = 6.1 Hz, $CH_2$), 2.89 (t, 2H, $J$ = 6.3 Hz, $CH_2$), 2.99 (s, 3H, N–$CH_3$), 3.35 (t, 2H, $J$ = 7.3 Hz, N–$CH_2$), 6.68 (d, 2H, $J$ = 8.9 Hz, Ar–H), 7.22 (s, 1H, C=C–H), 7.35 (d, 2H, $J$ = 8.9 Hz, Ar–H), 7.63 (d, 1H, $J$ = 6.5 Hz, Ar–H), 8.37 (m, 3H, Ar–H).

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