

Two-dimensional characteristics of the second-order nonlinear optical response in dipolar donor–acceptor coordination complexes†

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The two-dimensional (2D) nonlinear optical (NLO) response of a series of dipolar donor–acceptor bis(salicylaldiminato)Ni(II) Schiff base planar coordination complexes was investigated using the INDO/SOS formalism. The in-plane 2D NLO character of this class of materials can be related to various low-energy charge-transfer (CT) states and is achieved by an accurate design of substitution pattern of the unsubstituted bis(salicylaldiminato) framework. While *z*-polarised electronic transitions, *parallel* with respect the molecular dipolar (*z*) axis, contribute to the diagonal hyperpolarisability tensor component, *perpendicular* *x*-polarised transitions contribute to off-diagonal hyperpolarisability tensors. Unlike non-dipolar multidimensional NLO structures, whose nonlinearity within the framework of the sum-over-states formalism is necessarily due only to three-level terms, in this case the 2D nonlinearity is generally dominated by two-level terms. It necessarily requires the existence of a strong, lowest energy, *perpendicular* CT transition in order to provide a substantial two-level contribution to off-diagonal tensors.

Intense research activity is currently associated with the synthesis and development of molecule-based second-order nonlinear optical (NLO) materials.^{1–3} Beside classical dipolar NLO chromophores, whose second-order molecular nonlinearity, β_{ijk} , is mostly one-dimensional (1D) in character (*i.e.*, dominated by one hyperpolarisability tensor component), in recent years non-dipolar molecular structures, having multidimensional (*n*D) NLO characteristics, have emerged as possible candidates for second-order NLO applications.^{2a,4,5} Compared to 1D dipolar chromophores, they offer the advantage of a better nonlinearity/transparency trade-off^{2a,4,5} and favour the formation of noncentrosymmetric architectures, due to the absence of a permanent dipole moment.⁶

Among second-order NLO materials, poled polymer thin films containing NLO chromophores have recently been widely investigated for photonic devices such as frequency converters or electro-optic modulators.^{1,2,7,8} Poling involves the application of an electric field to the polymer film, which causes partial alignment of the NLO-active chromophores and induces an acentric microstructure. While this standard poling technique is well-suited for dipolar NLO chromophores,⁷ the poling of non-dipolar structures represents a current challenge solved, to date, only for some suitable classes of non-dipolar NLO chromophores by the “optical poling” technique.^{4a,9}

In principle, dipolar multidimensional NLO chromophores combine the advantages of dipolar and nondipolar chromophores. In the case of poled polymer applications, the ability of 2D dipolar chromophores to retain second-order optical nonlinearity, even if “orientationally relaxed”, was demonstrated.¹⁰ Moreover, they would provide polarisation-independent materials if used in thin film devices for electro-optical applications.^{11,12}

Very few examples of dipolar second-order *n*D NLO chromophores have been reported in the literature, with most of

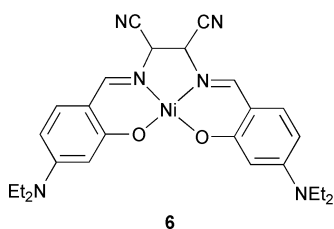
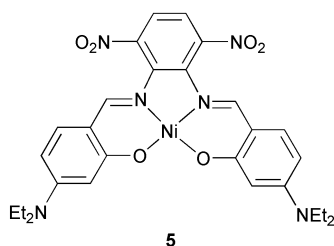
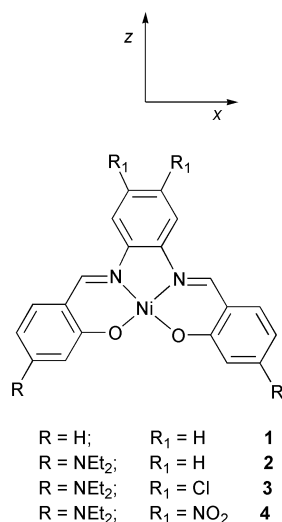
them based on benzene derivatives.^{13,14} In this paper we report the design and a detailed theoretical analysis, using the INDO/S-SOS quantum chemical formalism,^{15,16} of a series of dipolar donor–acceptor bis(salicylaldiminato)Ni(II) complexes (Scheme 1), having in-plane two-dimensional NLO character. Although the second-order NLO properties of some of the present complexes have been previously investigated,^{17,18} we emphasise that the goal of this investigation is to probe the effects of donor–acceptor substituents on the in-plane two-dimensional NLO character of this novel class of 2D NLO materials.

Theoretical method

Within the framework of the sum-over excited particle-hole-states (SOS) perturbation theory, the molecular quadratic hyperpolarisability, for instance second harmonic generation, $\beta_{ijk}(2\omega; \omega, \omega)$, can be related exactly to all the excited states of the molecule in terms of their energy, $\hbar\omega_{ng}$, transition dipole moment, r_{gn}^i , and dipole moment variation, $\Delta r_n^i = r_{nn}^i - r_{gg}^i$, between ground (g) and excited (n) states [eqn. (1)].¹⁹

$$\begin{aligned} \beta_{ijk}(-2\omega; \omega, \omega) &= -\frac{e^3}{4\hbar^2} \left[\sum_{n \neq g} \sum_{\substack{n' \neq g \\ n' \neq n}} \left\{ (r_{gn}^j r_{n'n}^i r_{gn}^k + r_{gn}^k r_{n'n}^j r_{gn}^i) \right. \right. \\ &\quad \times \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right] \\ &\quad + (r_{gn}^j r_{n'n}^i r_{gn}^k + r_{gn}^i r_{n'n}^j r_{gn}^k) \\ &\quad \times \left[\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right] \\ &\quad + (r_{gn}^j r_{n'n}^k r_{gn}^i + r_{gn}^k r_{n'n}^j r_{gn}^i) \\ &\quad \times \left. \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right] \right\} \end{aligned}$$

† Electronic supplementary information (ESI) available: optimised Cartesian co-ordinates for structures 2–6. See <http://www.rsc.org/suppdata/nj/b1/b108672c/>



Scheme 1

$$+ 4 \sum_{n \neq g} \left\{ [r_{\text{gn}}^j r_{\text{gn}}^k \Delta r_n^i (\omega_{\text{ng}}^2 - 4\omega^2) + r_{\text{gn}}^j (r_{\text{gn}}^k \Delta r_n^j + r_{\text{gn}}^j \Delta r_n^k) \times (\omega_{\text{ng}}^2 + 2\omega^2)] \times \frac{1}{(\omega_{\text{ng}}^2 + \omega^2)(\omega_{\text{ng}}^2 - 4\omega^2)} \right\} \quad (1)$$

The hyperpolarisability determined by a sum-over-states expression can be partitioned into two contributions,¹⁵ so-called two-level ($\beta_{ijk,2}$) terms [enclosed in the second set of braces in eqn. (1)] and three-level ($\beta_{ijk,3}$) terms [enclosed in the first set of braces in eqn. (1)], such that: $\beta_{ijk}(2\omega; \omega, \omega) = \beta_{ijk,2} + \beta_{ijk,3}$. Each two-level component in the sum for $\beta_{ijk,2}$ contains only two states, the ground state plus one excited state and is related to the product $r_{\text{gn}}^j r_{\text{gn}}^k \Delta r_n^i$ (generic two-level term); while the three-level contributions involve the ground state and two excited states, n, n' , and are related to the product $r_{\text{gn}}^j r_{\text{n'n}}^i r_{\text{gn}}^k$ (generic three-level term). Moreover, analysis of term contributions to the molecular hyperpolarisability for each excited state, the so-called “state-by-state” analysis, allows one to understand the variables influencing β_{ijk} and its dependence upon the molecular electronic properties. For dipolar molecules, the molecular hyperpolarisability is generally related to the β_μ value, that is the vector component of the β_{ijk} tensor along the dipole moment direction, given by: $\beta_\mu = \sum_{i=1}^3 \mu_i \beta_i / |\mu|$, where μ is the ground state dipole

moment and $\beta_i = \beta_{iii} + 1/3 \sum_{j \neq i} (\beta_{ijj} + \beta_{jij} + \beta_{jjj})$. Another quantity of interest is the intrinsic total hyperpolarisability, β_{vec} , given by: $\beta_{\text{vec}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$.

For most dipolar molecules, in which Δr_n^i and r_{gn}^i matrix elements are parallel to the dipolar i axis, the $\beta_{ijk,2}$ sum generally dominates the NLO response, resulting in 1D dipolar species with a single hyperpolarisability diagonal tensor component β_{iii} , so that: $\beta_{\text{vec}} \cong \beta_i$ and hence, $\beta_\mu \cong \beta_{iii}$. On the other hand, only nonzero, off the i diagonal, dipole moment (Δr_n^i ; $j \neq i$) or transition dipole moment ($r_{\text{n'n}}^i$; $j \neq i$) matrix elements, contribute to the off-diagonal β_{ijk} hyperpolarisability tensor components. For dipolar molecules of C_{2v} symmetry, β has seven non-vanishing tensor components, five of which are independent. The nonzero components are β_{zzz} , $\beta_{xzx} = \beta_{xxz}$, β_{zxx} , $\beta_{yzy} = \beta_{yyz}$, β_{zyy} , where z is the C_2 axis. Since transition dipole moments perpendicular to the zx molecular plane are generally small, the components $\beta_{yzy} = \beta_{yyz}$ and β_{zyy} are usually negligible. Thus, the parameter $u = \beta_{\text{off-diagonal}} / \beta_{zzz}$, where $\beta_{\text{off-diagonal}} = 1/3(\beta_{xzx} + \beta_{xxz} + \beta_{zxx})$, reflects the anisotropy of the in-plane optical nonlinearity.⁴

Computational details

The all-valence INDO/S (intermediate neglect of differential overlap) model,²⁰ in connection with the SOS formalism,¹⁹ was employed. Details of the computationally efficient ZINDO-SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.^{15,16} Standard parameters and basis functions were used.²⁰ In the present approach, the closed-shell restricted Hartree-Fock (RHF) formalism was adopted. The monoexcited configuration interaction (CIS) approximation was employed to describe the excited states. In all calculations, the lowest 150 energy transitions between SCF and CIS electronic configurations were chosen to undergo CI mixing and were included in the SOS. This SOS truncation was found to be sufficient for complete convergence of the second-order response in all cases considered. Non-resonant hyperpolarisability values are thus calculated within a perturbation series expansion employing the Ward definition,¹⁹ the so-called phenomenological convention.²¹ All calculations were performed using the ZINDO program^{15,16} implemented on an IBM SP system. The computed ground state dipole moment (μ_g) and second-order NLO response of the present molecules are collected in Table 1. Metrical parameters of **2–6** used for INDO/S calculations were taken from fully optimised structures at the ZINDO/1 level using the HyperChem package.²² A C_{2v} planar structure of the bis(salicylaldiminato) framework was always found in all cases presently considered.²³ Present optimised planar structures are consistent with crystallographic-derived planar structures for unsubstituted M(salophen) complexes,²⁴ as well as for the substituted donor-acceptor **4** derivative.¹⁷ Moreover, optimised geometrical parameters are in favourable agreement with available experimental values.^{17,24}

Results and discussion

Recently, bis(salicylaldiminato)M(II) Schiff base complexes have been developed as a new class of efficient second-order NLO materials.^{17,18} The optical nonlinearity of such complexes has generally been related to a low-energy charge-transfer (CT) transition, in which the metal acts as an electron donor, and thus has been described in terms of a two-state model.^{18c} Therefore, analogously to classical dipolar molecules, a single hyperpolarisability tensor component, β_{zzz} , parallel to the dipolar z axis of the molecule, dominates the NLO response of such materials.

Table 1 Computed ground state dipole moments and second-order NLO response^{a,b} for donor-acceptor Schiff base Ni(II) complexes

	μ_g/D	$\hbar\omega/eV$	β_{zzz}	$\beta_{xzx}=\beta_{xxz}$	β_{zxx}	u	β_{vec}	β_μ
1	8.5	0.0	-10.0	-1.5	-1.5	0.15	11.5	-11.5
		0.92	-16.1	-1.9	0.3	0.07	17.3	-17.3
2	3.2	0.0	-17.0	-7.3	-7.3	0.43	24.4	-23.8
		0.92	-25.3	-13.6	-8.7	0.47	37.2	-36.4
3	3.2	0.0	19.1	9.2	9.2	0.48	28.3	27.9
		0.92	29.3	17.8	11.5	0.54	45.1	44.3
4^c	7.7	0.0	66.1	0.1	0.1	0.00	66.2	65.8
		0.92	145.8	-5.9	-12.1	0.05	137.5	137.1
5^c	1.2	0.0	30.0	13.0	13.0	0.43	43.0	36.5
		0.92	46.9	25.3	16.9	0.48	69.1	58.9
6^c	5.0	0.0	19.8	19.7	19.6	0.99	39.5	39.1
		0.92	30.5	44.8	29.3	1.30	70.2	69.7

^a In $10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. Nonresonant hyperpolarizability values are given in the phenomenological convention, where β_{ijk} are by a factor of $1/4$ smaller than in the Taylor series convention (see ref. 21). ^b For definition of parameters, see text. ^c Computed μ_g and β_μ data for compounds **4–6** are different from those previously reported,^{17,18c,d} because of the presently adopted optimised geometrical parameters and/or different number of CIS configurations (see Computational details).

Unsubstituted bis(salicylaldiminato) complexes, such as the M(salophen) (N,N' -disalicylidene-1,2-phenylenediaminato)-M(II), possess a C_{2v} symmetry, with the C_2 axis lying along the molecular dipolar axis.^{24a,b} Among the relevant optical transitions in the UV-visible region, both the “in-plane” z-polarised and x-polarised transitions are allowed. They involve absorption of radiation with its electric vector vibrating, respectively, *parallel* and *perpendicular* with respect to the molecular dipolar axis (Scheme 2). Actually, both types of electronic transitions are predicted in the UV-vis region for the prototypical compound Ni(salophen) (**1**) (Table 2). In particular, a relatively weak, x-polarised, perpendicular transition is associated with the lowest energy CT excited state, followed by a relatively intense, z-polarised, parallel CT transition, and then by a relatively weak perpendicular transition. Both perpendicular and parallel transitions are associated with the higher energy excited states.

The calculated second-order nonlinearity for **1** indicates that the nonzero β_{ijk} tensor components are β_{zzz} , β_{zxx} , and $\beta_{xzx}=\beta_{xxz}$; the off-diagonal terms are about 90% smaller than the diagonal one, β_{zzz} (Table 1). Since this molecule possesses a C_{2v} symmetry, only diagonal dipole moment matrix elements, parallel to the dipolar z axis, are predicted ($\Delta r_n^i \neq 0$; $i=z$). Therefore, off-diagonal hyperpolarisability tensor terms are related only to perpendicular transition dipole moment (r_n^j ; $j \neq i$) elements. However, since the intensities of these perpendicular transitions are relatively low, the resulting off-diagonal β_{ijk} tensor terms are smaller than the β_{zzz} tensor ($\beta_{zzz} = -16.1 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$; $\beta_{\text{off-diagonal}} = -1.2 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$; $\hbar\omega = 0.92 \text{ eV}$), thus resulting in a predominantly 1D NLO character ($\beta_{vec} \cong \beta_{zzz}$; $u \leq 0.1$). Moreover, the state-by-state analysis indicates that a single state (S2) is principally responsible for the nonlinearity (Table 2).

On these grounds, it can be predicted that dipolar planar molecular architectures possessing intense low-energy *perpendicular* CT transitions would result in materials having large off-diagonal hyperpolarisability tensor components. Use of appropriate substitution patterns in **1** is thus expected to enhance such perpendicular CT transitions and, hence, the 2D character of such materials.

As a first example we consider the 4-diethylamino donor substitution on the salicylidene rings (**2**).²⁵ Analogously

to **1**, the ground state dipole moment of **2** is directed between the imine groups. In this case, however, the strong electron-donor capability of the diethylamino substituents tends to counter-balance the charge separation compared to the unsubstituted complex **1**, thus resulting in a reduced dipole moment (Table 1). Analogously to **1**, perpendicular and parallel CT electronic transitions are associated with the lowest excited states. These transitions are more intense than those of **1** and result in an enhanced optical nonlinearity ($\beta_{vec} = 37.2 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$; $\hbar\omega = 0.92 \text{ eV}$) and in a sizeable 2D NLO character of **2** ($u = 0.47$). In contrast to **1**, many states clearly contribute to the optical nonlinearity. The state-by-state analysis (Table 2) allows us to evaluate the contribution of each excited state to the β_{ijk} components. In particular, the nonlinearity of **2** can be mainly related to the three lowest energy CT excited states (S1–S3). Transition dipole moment elements associated with these states are, respectively, perpendicular, parallel and perpendicular. Moreover, since this molecule possesses a C_{2v} symmetry ($\Delta r_n^i = 0$; $j \neq z$) analogously to **1** only perpendicular transition dipole moment elements will contribute to the off-diagonal tensor components. In fact, while the S2 state contributes to β_{zzz} ($\approx 44\%$ of the two-level $\beta_{zzz,2}$ sum), the S1 and S3 states

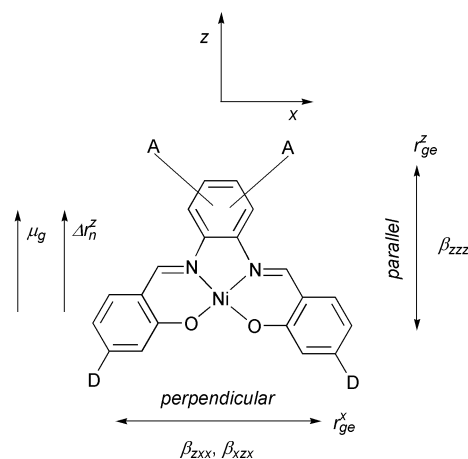
**Scheme 2**

Table 2 Computed linear optical spectroscopic and state-by-state analysis of the static second-order NLO response (10^{-30} cm⁵ esu⁻¹) for **1–6**

State	Symmetry(polarisation)	$\hbar\omega_{eg}/\text{eV}$	r_{ge}^z/D	r_{ge}^x/D	$\Delta r_n^z/D$	$\beta_{zzz,2}$	$\beta_{zzz,3}$	$\beta_{zxx,2}$	$\beta_{zxx,3}$	$ \beta_z $
Compound 1										
S1	B ₁ (x)	3.02	0.00	3.45	-3.27	0.0	0.0	-0.8	0.0	0.8
S2	A ₁ (z)	3.21	5.97	0.00	-5.22	-11.2	0.0	0.0	0.4	10.8
S3	B ₁ (x)	3.42	0.0	-2.73	-1.05	0.0	0.0	-0.1	-0.8	0.9
S4	A ₁ (z)	3.63	-0.11	0.00	-4.99	0.0	0.0	0.0	0.0	0.0
$\sum_n S_n$						-14.7	4.7	-4.7	3.2	11.5
Compound 2										
S1	B ₁ (x)	2.95	0.00	6.37	-1.66	0.0	0.0	-1.5	0.0	1.5
S2	A ₁ (z)	3.23	7.19	0.00	-3.58	-10.4	0.0	0.0	0.7	9.7
S3	B ₁ (x)	3.48	0.00	6.84	-4.73	0.0	0.0	-3.5	-4.0	7.5
$\sum_n S_n$						-23.8	6.8	-7.8	0.5	24.3
Compound 3										
S1	B ₁ (x)	2.93	0.00	-6.75	1.99	0.0	0.0	2.0	0.0	2.0
S2	A ₁ (z)	3.21	-7.55	0.00	3.63	11.7	0.0	0.0	-0.7	11.0
S3	B ₁ (x)	3.45	0.00	-6.71	6.27	0.0	0.0	4.4	5.0	9.4
$\sum_n S_n$						29.2	-10.1	9.0	0.2	28.3
Compound 4										
S1	B ₁ (x)	2.33	0.00	2.88	7.52	0.0	0.0	2.2	0.0	2.2
S2	A ₁ (z)	2.80	10.15	0.00	14.34	110.1	0.0	0.0	-11.7	98.4
S3	B ₁ (x)	2.86	0.00	7.11	5.61	0.0	0.0	6.7	-9.3	2.6
$\sum_n S_n$						122.2	-56.1	22.7	-22.6	66.2
Compound 5										
S3	B ₁ (x)	2.95	0.0	7.19	3.39	0.0	0.0	3.9	0.0	3.9
S8	A ₁ (z)	3.21	7.70	0.0	3.77	12.7	3.2	0.0	0.5	16.4
S10	B ₁ (x)	3.43	0.0	5.88	7.95	0.0	0.0	4.6	4.9	9.5
S12	A ₁ (z)	3.46	5.88	0.0	7.95	12.1	-0.9	0.0	-5.3	5.9
$\sum_n S_n$						39.9	-9.9	12.7	0.3	43.0
Compound 6										
S1	B ₁ (x)	2.69	0.0	-9.11	3.09	0.0	0.0	6.8	0.0	6.8
S2	A ₁ (z)	3.12	5.71	0.00	5.91	11.6	0.0	0.0	6.1	17.7
S4	B ₁ (x)	3.32	0.0	-5.82	6.93	0.0	0.0	4.1	4.4	8.5
S6	A ₁ (z)	3.74	-6.80	0.00	7.85	15.2	-4.8	0.0	4.4	15.6
$\sum_n S_n$						33.3	-13.5	15.8	3.9	39.5

account for the off-diagonal tensor components ($\approx 64\%$ of the two-level $\beta_{\text{off-diagonal},2}$ sum). In addition, since these excited states involve a decrease of the dipole moment with respect to the ground state ($\Delta r_n^z < 0$), negative hyperpolarisability values are calculated (Table 1).

Enhanced diagonal and off-diagonal optical nonlinearity is predicted for the donor-acceptor structure **3** (Table 1), obtained from **2** by a 4,5-dichloro phenylene ring substitution. This is due to both the larger dipole moment and transition dipole moment values associated with the main excited states involved (S1–S3) (Table 2). Moreover, in contrast to **2**, positive hyperpolarisabilities are calculated for **3** because of the increased dipole moments associated with these excited states ($\Delta r_n^z > 0$). In this molecule, the dipole moments of the ground and excited states are both directed between the oxygen donor atoms. The presence of the chlorine acceptor substituents leads to the opposite direction of the ground state dipole moment, compared to **2**. Analogously to **2**, the off-diagonal nonlinearity of **3** is dominated by the two-level sum, the three-level sum being almost negligible. This is in marked contrast with non-dipolar nD NLO chromophores, the NLO response of which is necessarily related to three-level terms.^{4,5,26} Previous theoretical analysis on simpler dipolar 2D chromophores was limited to the discussion of the global β_{ijk} tensor components without individual excited state involvement,^{14b} or analysed by simplified sum-over-states calculations.^{14c,d}

The above findings are fully supported by experimental data. HRS measurements of **3** indicate²⁷ β_{ijk} values ($\beta_{zzz} = 43 \times 10^{-30}$ cm⁵ esu⁻¹; $\beta_{\text{off-diagonal}} = 20 \times 10^{-30}$ cm⁵ esu⁻¹; $\hbar\omega = 0.92$ eV) in favourable agreement with the present theoretical values ($\beta_{zzz} = 29.3 \times 10^{-30}$ cm⁵ esu⁻¹; $\beta_{\text{off-diagonal}} = 15.7 \times 10^{-30}$ cm⁵ esu⁻¹; $\hbar\omega = 0.92$ eV). Moreover, the experimental data²⁷ indicate an in-plane NLO anisotropy ($u = 0.47$) in very good agreement with the calculated ($u = 0.54$) value.

On this basis, it could be expected that replacement of the two weak chlorine acceptor groups in **3** by two strong electron-acceptor groups, such as nitro groups, (**4**), would imply a further enhancement of the 2D NLO character of such materials. Actually, even if the optical nonlinearity of **4** is strongly enhanced relative to **3** (Table 1) it derives mainly from the diagonal β_{zzz} tensor ($\beta_{zzz} = 145.8 \times 10^{-30}$ cm⁵ esu⁻¹; $\hbar\omega = 0.92$ eV) and, hence, results in a predominantly 1D NLO character ($\beta_{\text{vec}} \cong \beta_{zzz}$; $u \leq 0.05$).²⁸ This is because even if the contribution of the three-level sum to the off-diagonal tensor components is larger than in **2** and **3** (Table 2), it is of opposite (negative) sign to the two-level sum, thus resulting in an almost vanishing off-diagonal tensor term. The state-by-state analysis again indicates that the three lowest energy states (S1–S3), the associated transition dipole moments of which have the same polarisations as in **2** and **3**, are mainly responsible for the optical nonlinearity. Compared to **3**, S1–S3 are characterised by a lower excitation energy, $\hbar\omega_{eg}$, and larger dipole moment variation, Δr_n^z , values for S1 and S2. Moreover, while the transition dipole moment values associated with the S2 and S3 states are larger than those of **3**, the lowest S1 state has a smaller perpendicular transition dipole moment. However, while states S1 and S3 give a positive two-level contribution to the off-diagonal tensor components, the S2 and S3 states contribute to even larger and negative three-level terms, which counterbalance the positive two-level sums, thus leading to the anticipated vanishing off-diagonal tensors (Table 2).

If the 4,5-nitro acceptor phenylene ring substitution leads to a 1D NLO character because of the resulting, predominant parallel low-energy CT transitions, the 3,6-nitro phenylene ring substitution (**5**) is expected to favour perpendicular low-energy CT transitions. In fact, molecule **5** shows a further enhanced optical nonlinearity, relative to **3**, even if the in-plane NLO anisotropy ($u \cong 0.48$) remains almost constant, as in **2** and **3** (Table 1,2).

These observations suggest that optimisation of the off-diagonal optical nonlinearity in such dipolar systems necessarily implies the existence of a strong, lowest energy, perpendicular CT transition in order to make a substantial two-level contribution to the off-diagonal tensors. As a matter of fact, the largest 2D character in such dipolar bis(salicylaldiminato)Ni(II) Schiff base complexes is achieved in the donor-acceptor complex **6** (Table 1). In fact, comparable off-diagonal ($\beta_{\text{off-diagonal}} = 39.6 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$; $\hbar\omega = 0.92 \text{ eV}$) and diagonal ($\beta_{zzz} = 30.5 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$; $\hbar\omega = 0.92 \text{ eV}$) hyperpolarisability tensor components are predicted for this molecule, with an almost in-plane NLO isotropy ($u = 1.3$). Off-diagonal tensor components of **6** derive principally ($\approx 80\%$) from the two-level sum; however, contrary to previous cases, the three-level sum contributes also ($\approx 20\%$) to the off-diagonal optical nonlinearity (Table 2). The state-by-state analysis indicates that the lowest energy S1 CT state, whose associated large transition dipole moment has a perpendicular polarisation, is the main contributor ($\approx 43\%$) to the two-level $\beta_{\text{off-diagonal},2}$ sum. This is a confirmatory example that the off-diagonal optical nonlinearity in such dipolar molecules mostly depends upon characteristics of the lowest energy CT state. Higher energy states contribute to the three-level terms, which sum positively to off-diagonal tensor components.

Summary and conclusions

This paper explores the two-dimensional characteristics of the NLO response of a class of dipolar planar donor-acceptor coordination complexes. The in-plane 2D optical nonlinearity of such compounds is related to various low-energy CT states. While z -polarised electronic transitions, *parallel* with respect to the molecular dipolar (z) axis, contribute to the diagonal β_{zzz} tensor, *perpendicular* x -polarised transitions contribute to the off-diagonal β_{ijk} hyperpolarisability tensors (Scheme 2). Unlike non-dipolar nD NLO structures, whose nonlinearity within the framework of the sum-over-states formalism is due only to three-level terms, in our case it is generally dominated by the two-level terms. Compared to dipolar 2D NLO chromophores reported in the literature,¹³ the present materials possess comparable or even larger non-resonant β_{ijk} values.

Large 2D optical nonlinearity in such dipolar systems can be achieved by accurate design of the substitution pattern of the unsubstituted bis(salicylaldiminato) framework, and necessarily implies the existence of an intense, lowest energy *perpendicular* CT transition in order to make a substantial two-level contribution to the off-diagonal tensors. The lowest energy state of these materials is thus always characterised by an intense x -polarised perpendicular CT transition. This implies that frequency-doubled photons through the off-diagonal β_{ijk} components would be polarised perpendicular with respect to the x -polarised transition dipole moment. Therefore, in a perfectly ordered array of such species, they will not be reabsorbed by the system. On the other hand, compared to conventional 1D chromophores, such materials are attractive candidates for poled polymer thin film SHG applications and in the perspective of electro-optic polarisation-independent materials for optical communication systems.

Studies are currently in progress to include these molecules in main-chain copolymers and to find other classes of dipolar 2D chromophores.

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