JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Nonlinear Optical Molecular Switches as Selective Cation Sensors

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Supporting Information

ABSTRACT: This work demonstrates that the recognition of cations by molecular switches can give rise to large contrasts of the second-order nonlinear optical (NLO) properties, which can therefore be used as a powerful and multi-usage detection tool. The proof of concept is given by evidencing, by means of ab initio calculations, the ability of spiropyran/merocyanine systems to selectively detect alkali, alkaline earth, and transition-metal cations.

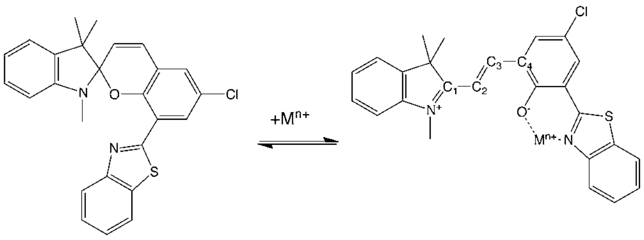
Detecting cations is of broad interest to chemists, clinical biochemists, toxicologists, and environmentalists, and therefore the elaboration of sensors constitutes an important challenge.[1] Generally the detection is based on changes of light absorption, i.e., on color variations or on the induction or modification of fluorescence. In this communication we demonstrate that a selective cation recognition can be performed by using molecular nonlinear optical (NLO) switches, i.e., by probing the change in the second-order NLO properties along the commutation processes. Indeed, these processes are accompanied by large NLO contrasts that depend on the nature of the cation involved, which therefore provides a powerful detection tool.

Besides the intrinsic interest for NLO, which encompasses frequency doubling and intensity-dependent refractive indices,[2] the NLO responses of molecules, supramolecules, and materials are properties that can be probed for characterization and detection purposes. So, second-order NLO is employed to highlight the nucleation and growth of nanocrystals and nanoparticles,[3] in second harmonic (SH) imaging spectroscopy,[4] as well as to monitor the conformational structure and dynamics of synthetic and natural polymer chains.[5] SH and sum frequency generation spectroscopies are also broadly employed to address surface structure and dynamics.[6] Moreover, recent works have evidenced the relationship between the SH response and the size and shape of metal and metal oxide nanoparticles, demonstrating also their ability for chemical process monitoring, biological and chemical sensing.[7]

Advantages of second-order NLO responses over linear optical responses come from the rich content of the second-order nonlinear susceptibility, $\chi^{(2)}$, or of its molecular equivalent, the first hyperpolarizability, β, which are rank 3 tensors containing more detailed, though more complex, material and molecular fingerprints. For instance, owing to this complexity, the apolar methane molecule presents a first hyperpolarizability but no permanent dipole moment,[8] while chiral molecules and architectures also display specific second-order responses.[5a,9] NLO switches are compounds characterized by their ability to alternate between two or more different chemical forms displaying contrasts in one of their NLO properties, generally the second harmonic generation (SHG) intensity. Such commutable systems, which are triggered either by light,[10] temperature,[11] pH,[12] or redox potential,[13] are exploited in optoelectronic applications, such as optical memories with multiple storage and nondestructive capacity.[14]

The concept of NLO-based detection of cations proposed here extends the domain of application of NLO switches. The proof of concept is given by considering a spiro[indoline-8-(benzothiazol-2-yl)-benzopyran] derivative (Scheme 1), already known for its metallochromic properties.[15] We show that the commutation is associated with an important β contrast when the merocyanine form complexes a collection of monovalent and divalent metal cations. In addition, it is demonstrated that the β contrasts depend strongly on the nature of the metal, providing a key for selective sensing.

Scheme 1. Equilibrium between the Spiropyran Form and Its Merocyanine Alter Ego Complexing a Cation



The proof of concept relies on computational chemistry experiments carried out by employing density functional theory for geometry optimization with the M06 exchange−correlation functional[16] and the 6-311G(d) basis set in combination, for performing the β calculations, with the finite field method based on the second-order Møller−Plesset (MP2) level of approximation and the time-dependent Hartree−Fock method using the 6-311+G(d) basis set. Additional excitation energy calculations were performed within the time-dependent density

Received: March 11, 2012
Published: May 1, 2012

functional theory (TDDFT) using the ωB97X functional.[17] Bulk solvent effects were accounted for within the integral equation formalism of the polarizable continuum model (IEFPCM),[18] whereas few explicit solvent (acetonitrile) molecules were also included in the cavity to describe the metal ion complexation. The frequency dispersion of β is described within the multiplicative scheme.[19] The reliability of this global theoretical approach, of which the details are provided in the Supporting Information (SI), is substantiated by recent studies carried out at similar levels of approximation. In particular, some of these contributions have demonstrated the ability of these methods to design fluoroionophores as well as molecular switches presenting large contrasts of first hyperpolarizability.[20] All calculations were performed using the Gaussian 09 package.[21]

The reported first hyperpolarizability quantities correspond to those governing the hyper-Rayleigh scattering intensities, i.e., β_{HRS}. Hyper-Rayleigh scattering is the technique of choice for revealing cations complexations since it works equally well for neutral and charged species. Often, the total β_{HRS} response is analyzed in terms of its two contributions, originating from perpendicular light polarizations; the ratio between these two contributions, namely the depolarization ratio (DR), is a signature of the symmetry of the NLOphore.[2b]

Data in Table 1 show that β_{HRS} strongly increases upon going from the closed spiropyran form to the open merocyanine form complexing the metal cations. The largest variations and largest β_{HRS} amplitudes appear when complexing alkali atoms (Li^+, Na^+, and K^+) and then come the β_{HRS} of the dications in the order $Ca^{2+} > Mg^{2+} > Zn^{2+} > Ni^{2+}$. Another difference between the monocations and dications is the DR, which is larger for the dications, demonstrating that in the latter case, the NLOphores depart more from ideal one-dimensional structures for which DR = 5. Still, the orientation of the vector component of β remains similar and aligned along the donor–acceptor phenolate–indoline axis (Figure 1). These variations in β and DR can be rationalized in terms of structural and electronic parameters (Table 1): (i) with respect to the complexation of monovalent cations, the complexation of a divalent cation increases the bond length alternation (BLA) along the ethylenic bridge (see also SI), which is associated with a decrease of conjugation between the donor–acceptor groups and a smaller β response; (ii) the complexation reduces the donor character of the phenolate moiety, in particular with divalent cations; and (iii) the complexation of Ni^{2+} is stronger as evidenced by the larger amount of charge transferred from the metal to the organic compound, and the reduction of the N···O distance between the ligand heads (from 2.95 Å in the uncomplexed merocyanine to 2.68 Å in the Ni^{2+} complex). Additional thermochemistry characterizations also attribute to the Ni^{2+} complexation reaction a ΔH^0 value 5 kcal/mol larger than in the case of Mg^{2+} at 298 K.

Table 1. Molecular Properties as a Function of the Nature of the Complexed Metal Ion

	β_{HRS}[a]	DR	Q(M)[b]	BLA[c]	λ_{abs}[d]
spiro	2.5	2.84	–	–	294
Li^+	110	5.88	0.89	0.04	456
Na^+	101	5.22	0.94	0.03	461
K^+	98	5.24	0.95	0.03	463
Mg^{2+}	71	6.35	1.76	0.06	414
Ca^{2+}	92	6.07	1.80	0.05	432
Zn^{2+}	67	6.41	1.60	0.06	415
Ni^{2+}	51	6.30	1.18	0.07	392

[a] HRS first hyperpolarizability at 1064 nm in 10^{-30} esu within the T convention. [b] NBO charge in e on the metal atom. [c] Bond length alternation (Å) of the conjugated bridge between the indolino and phenolate rings, defined as BLA = $d_{12} - 2d_{23} + d_{34}$ (Scheme 1). [d] TDDFT/ωB97X/6-311G(d) vertical excitation energies in nm.

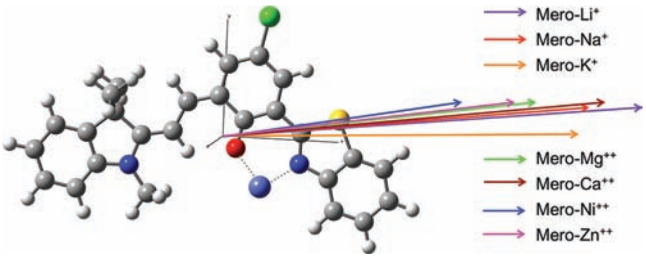


Figure 1. Vector component of the MP2 β as a function of the nature of the cation complexed by the merocyanine. Color code: carbon (gray), hydrogen (white), nitrogen (blue), oxygen (red), sulfur (yellow), chlorine (green), and the cation (light blue).

The complexation of cations also modifies the linear optical properties (and in particular the wavelength associated with the dominant lowest energy transition, λ_{abs}), as shown by the TDDFT results presented in Table 1, which reproduce the experimental data of ref 15b (going from the spiro to the Ni^{2+}-complex forms, the experimental maximum absorption shifts to the red by 1.03 eV, whereas the calculations predict a shift of the vertical excitation energy of 1.06 eV). These first transitions are dominated by HOMO to LUMO (LUMO+1 for Ni^{2+}) singly excited electronic configurations displaying charge-transfer character from the indolino to the phenolate rings (see SI). In the case of the dications, the λ_{abs} variations enable to a large extent to explain those of β within the two-state approximation: Larger β responses are associated to systems with smaller excitation energies. This does not hold for the alkali cations, which is attributed to a better charge transfer in the excited state for Li^+ owing to the out-of-plane position of the Na^+ and more markedly of the K^+ atoms. In general, the β contrasts are larger than the change of λ_{abs}, demonstrating an advantage of using the second-order NLO response as a detection mean but also giving credit to a two-dimensional detection of cations complexation.

These results evidence the large impact of the cation size and charge on the first hyperpolarizability. Moreover, these β variations upon cation complexation display stability with respect to the method of calculation as well as with respect to adding specific solvent molecules to complete the cation solvation shell. Indeed, within the IEFPCM treatment, two or four acetonitrile molecules were added around the Mg^{2+} cation (d_{Mg-N} = 2.15–2.23 Å), but β_{HRS} does not change by more than 1 and 3%, respectively.

In summary, we have given the proof of concept that second-order molecular switches can be used as efficient cation sensors, with abilities to discriminate between their size and charge, giving rise to improved selective cation detection by combining variations of the linear and nonlinear optical responses. Moreover, the photochromic properties of these benzothiazole benzopyran compounds can be used to commute from the complexed form back to the spiropyran species, providing reusable probes for environment monitoring. Similarly, one can take advantage of the spiropyran to merocyanine photoswitching to modify the probing efficiency of the ligands, broadening the scope and the efficiency of the cation detection.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of the computational procedure, atomic Cartesian coordinates of the optimized molecular structures and corresponding M06 energies, and frontier orbitals of the singly excited configurations describing the lowest energy absorption peak. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.P. is grateful to the F.R.S.-FNRS for her postdoctoral researcher position and B.C. to BELSPO (IAP network 'Functional Supramolecular Systems') for financial support. The calculations were performed on the Interuniversity Scientific Computing Facility (ISCF) installed at the FUNDP, for which we gratefully acknowledge the financial support from the F.R.S.-FRFC (convention no. 2.4.617.07.F) and from the FUNDP.

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