The effect of the cobalt and manganese central metal ions on the nonlinear optical properties of tetra (4-propargyloxyphenoxy) phthalocyanines

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DFT calculations for NLO properties

DFT calculation of hyper-Rayleigh Scattering (HRS) response coefficient (β_{HRS}) is carried out in order to calculate the first static hyperpolarizability, following literature method [**1-6**]. The advantage of this method is that octupolar and dipolar second order NLO contributions are theoretically separated. The major contribution to the total β_{HRS} is known to be largely controlled by the octupolar contribution [**1,2**]. The values of both dipolar ($\beta_{J=1}$) and octupolar ($\beta_{J=3}$) are known to be significantly influenced by the number of electrons in the system [**1**]. Due to symmetry constraints there is no permanent dipole moment for octupolar molecules [**5**], hence octupolar molecules present an isotropic β tensor.

It is to be noted that the equations presented below are only valid in the off-resonance region [**7**]. The following equations were used to calculate the (β_{HRS}) response. In **Equation 1**, $\langle \beta_{ZZZ}^2 \rangle$ and $\langle \beta_{ZXX}^2 \rangle$ are the orientation average of the molecular β tensor components.

$$\beta_{HRS}(-2\omega;\omega,\omega) = (\langle \beta_{ZZZ}^2 \rangle + (\langle \beta_{ZXX}^2 \rangle)^{1/2} \qquad \textbf{(1)}$$

The molecular β tensor were calculated using **Equations 2** and **3** [**7**]:

$$\langle \beta_{ZZZ}^2 \rangle = \frac{1}{7}\sum_{\zeta}^{x,y,z} \beta_{\zeta\zeta\zeta}^2 + \frac{6}{35}\sum_{\zeta \neq \eta}^{x,y,z} \beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta} + \frac{9}{35}\sum_{\zeta \neq \eta}^{x,y,z} \beta_{\eta\zeta\zeta}^2 + \frac{2}{3}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z} \beta_{\zeta\eta\xi}^2 \qquad (2) \quad + \frac{3}{35}$$

$$\langle \beta_{ZXX}^2 \rangle = \frac{1}{35}\sum_{\zeta}^{x,y,z} \beta_{\zeta\zeta\zeta}^2 - \frac{2}{105}\sum_{\zeta \neq \eta}^{x,y,z} \beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta} + \frac{11}{105}\sum_{\zeta \neq \eta}^{x,y,z} \beta_{\eta\zeta\zeta}^2 \qquad (3)$$

$$-\frac{1}{105}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\eta\xi\xi}+\frac{4}{105}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\zeta\eta\xi}^{2}$$

In addition, the molecular geometric information is given by the depolarization ratio (DR), which is expressed by $DR = \langle\beta_{ZZZ}^{2}\rangle/\langle\beta_{ZXX}^{2}\rangle$. The nature of the symmetric Rank-3 β tensor is further clarified by decomposing $\langle\beta_{HRS}^{2}\rangle$ as the sum of the dipolar ($\beta_{J=1}$) and octupolar ($\beta_{J=3}$) tensorial components [**5**], which are expressed as **Equation 4 to 6**:

$$\beta_{HRS} = \sqrt{\langle\beta_{HRS}^{2}\rangle} = \sqrt{\frac{10}{45}|\beta_{J=1}|^{2}+\frac{10}{105}|\beta_{J=3}|^{2}} \qquad (4)$$

$$|\beta_{J=1}|^{2} = \frac{3}{5}\sum_{\zeta}^{x,y,z}\beta_{\zeta\zeta\zeta}^{2}+\frac{6}{5}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta}+\frac{3}{5}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\eta\zeta\zeta}^{2}+\frac{3}{5}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\eta\xi\xi} \qquad (5)$$

$$|\beta_{J=3}|^{2} = \frac{2}{5}\sum_{\zeta}^{x,y,z}\beta_{\zeta\zeta\zeta}^{2}-\frac{6}{5}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta}+\frac{12}{5}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\eta\zeta\zeta}^{2}-\frac{3}{5}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\eta\xi\xi} \qquad (6)$$

$$+\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\zeta\eta\xi}^{2}$$

The ratio of octupolar $[\Phi_{J=3} = \rho/(1+\rho)]$ and dipolar $[\Phi_{J=1} = 1/(1+\rho)]$ contribution to the hyperpolarizability tensor is determined by substituting the nonlinear anisotropy parameter $\rho = |\beta_{J=3}|/|\beta_{J=1}|$ [**5**]. The nonlinear anisotropy parameter values run from 0 (pure dipole) to ∞ (pure octupole).

The theoretical normalized HRS intensity ($I_{\Psi V}^{2\omega}$) is determined by using Bersohn's expression [**5**], **Equation 7**, which assumes a general elliptically polarised incident light propagating along the X direction. **Equation 7** further assumes that the intensity of the harmonic light is scattered at 90° along the Y direction and the vertically (V) polarised light along the Z axis.

$$I_{\Psi V}^{2\omega} \propto \langle\beta_{ZXX}^{2}\rangle cos^{4}\Psi + \langle\beta_{ZZZ}^{2}\rangle sin^{4}\Psi + sin^{2}\Psi cos^{2}\Psi \times \langle(\beta_{ZXZ}+\beta_{ZZX})^{2}-2\beta_{ZZZ}\beta_{ZXX}\rangle \qquad (7)$$

The orientational averages $\langle(\beta_{ZXZ}+\beta_{ZZX})^{2}-2\beta_{ZZZ}\beta_{ZXX}\rangle$ in **Equation 7** is expressed as **Equation 8**:

$$\langle(\beta_{ZXZ}+\beta_{ZZX})^{2}-2\beta_{ZZZ}\beta_{ZXX}\rangle = 7\langle\beta_{ZXX}^{2}\rangle-\langle\beta_{ZZZ}^{2}\rangle = \frac{2}{35}\sum_{\zeta}^{x,y,z}\beta_{\zeta\zeta\zeta}^{2}-\frac{32}{105}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta}+\frac{10}{21}\sum_{\zeta \neq \eta}^{x,y,z}\beta_{\eta\zeta\zeta}^{2} \qquad (8)$$

$$-\frac{16}{105}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\eta\xi\xi}+\frac{22}{105}\sum_{\zeta \neq \eta \neq \xi}^{x,y,z}\beta_{\zeta\eta\xi}^{2}$$

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