

Supporting Information

Replacing Carbazole with [2.2]Paracyclophane and Triptycene Donors: Theoretical Insights into the Modulation of Second-order Nonlinear Optical Properties

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Computational details

The separation of the exchange term into a short-range DFT and a long-range HF is defined by the interelectronic distance r_{12} and the error function $\text{erf}(x)$ ¹ as following formula:

$$r_{12}^{-1} = r_{12}^{-1} \text{erfc}(\omega r_{12}) + r_{12}^{-1} \text{erf}(\omega r_{12}) \quad (1)$$

The range-separation parameter ω represents the inverse of the distance at which the exchange changes from DFT-like to HF-like. In exact Kohn–Sham (KS) theory, the negative HOMO energy $-\varepsilon_{\text{H}}(N)$ for an N -electron system should be equal to the vertical ionization potential (IP). This optimal tuning method, in brief, is determined nonempirically through minimizing the following equation:

$$J = |\varepsilon_{\text{H}}(N) + \text{IP}(N)| \quad (2)$$

A more refined target functional as shown below was proposed particularly for “better” description of HOMO–LUMO gap or transport gap:

$$J^2 = \sum_{i=0}^1 [\varepsilon_{\text{H}}(N+i) + \text{IP}(N+i)]^2 \quad (3)$$

The above equation simultaneously applies the IP criterion for both neutral (N) and anion ($N+1$) systems.

Champagne et al² developed an effective method to evaluate the hyper-Rayleigh scattering (HRS) response $\beta_{\text{HRS}}(-2\omega; \omega, \omega)$. The second-order NLO response that can be extracted by Bersohn’s expression:

$$\beta_{\text{HRS}}(-2\omega; \omega, \omega) = \sqrt{\langle \beta_{\text{ZZZ}}^2 \rangle + \langle \beta_{\text{ZXX}}^2 \rangle} \quad (3)$$

while the associated depolarization ratio (DR), which reveals the shape of the NLO-phore, given by:

$$\text{DR} = \frac{\langle \beta_{\text{ZZZ}}^2 \rangle}{\langle \beta_{\text{ZXX}}^2 \rangle} \quad (4)$$

$\langle \beta_{\text{ZZZ}}^2 \rangle$ and $\langle \beta_{\text{ZXX}}^2 \rangle$ are the orientational average of the molecular β tensor components without assuming Kleinman’s conditions^{3, 4}. Full expressions for the relationships between these averages (in the laboratory frame) and the molecular

tensor components (in the molecular frame) can be found in relative papers.⁵

$$\beta_{HRS} = \sqrt{(\beta_{HRS}^2)} = \sqrt{\frac{10}{45}|\beta_{J=1}|^2 + \frac{10}{105}|\beta_{J=3}|^2} \quad (5)$$

The $\beta_{J=1}$ and $\beta_{J=3}$ are the dipolar [$\Phi_{J=1} = 1/(1+\rho)$] and octupolar [$\Phi_{J=3} = \rho/(1+\rho)$] contributions to the HRS hyperpolarizability, respectively, where considered their absolute values. The relative contribution of the octupolar and dipolar components is given by the nonlinear anisotropy ratio $\rho = |\beta_{J=3}|/|\beta_{J=1}|$. Furthermore, assuming a general elliptically polarized incident light propagating along the X direction, with a state of polarization characterized by two angles (Ψ , δ), the intensity of the harmonic light scattered at 90° along the Y direction, and vertically (V) polarized (along the Z axis) is given by the Bersohn's expression^{4, 5}:

$$I_{\Psi V}^{2\omega} \propto \langle \beta_{ZXX}^2 \rangle \cos^4 \psi + \langle \beta_{ZZZ}^2 \rangle \sin^4 \psi + \sin^2 \psi \cos^2 \psi \langle (\beta_{ZZZ} + \beta_{ZZX})^2 - 2\beta_{ZZZ}\beta_{ZXX} \rangle \quad (6)$$

Table S1 The β_{tot} values ($\times 10^{-30}$ esu) of all studied molecules calculated at the ω B97XD/6-3+G(d) level.

	Compound	β_x	β_y	β_z	β_{tot}
	CzPhTrz	-26.2	0.3	-0.3	26.2
Gas	CzpPhTrz	-27.8	0.8	1.5	27.9
	TCz-Trz	-28.5	0.6	-1.7	28.6
	CzPhTrz	-31.7	0.4	-0.3	31.7
PCM	CzpPhTrz	-34.2	1.0	1.3	34.2
	TCz-Trz	-33.3	0.9	-2.0	33.4

Table S2 The β_{tot} values ($\times 10^{-30}$ esu) of all studied molecules calculated at the ω B97XD methods with different basis set.

Compound	6-31G(d,p)	6-311G(d,p)	6-3+G(d)	6-311+G(d,p)	6-311++G(d,p)
CzPhTrz	26.7	26.5	26.2	26.0	26.0
CzpPhTrz	28.7	27.9	27.9	27.7	27.7
TCz-Trz	28.9	29.0	28.6	28.6	28.6

Table S3 The β_{tot} values ($\times 10^{-30}$ esu) of all studied molecules calculated at the different methods with 6-31+G(d) basis set.

Compound	ω^* B97XD (ω^* , bohr $^{-1}$)	CAM- B3LYP	BHandHLYP	Toluene
CzPhTrz	36.3 (0.132)	30.6	29.3	31.7
CzpPhTrz	38.7 (0.135)	32.4	31.1	34.2
TCz-Trz	41.3 (0.128)	33.6	32.4	33.4

Table S4 The γ_{tot} values ($\times 10^5$ a.u.) of all studied molecules calculated at the $\omega\text{B97XD/6-3+G(d)}$ level in toluene.

Compound	γ_x	γ_y	γ_z	γ_{tot}
CzPhTrz	3.4	1.1	0.5	3.6
CzpPhTrz	3.8	1.2	0.6	4.0
TCz-Trz	3.8	1.5	1.0	4.2

References

1. T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett., 2004, 393, 51-57.
2. M. Guillaume, B. Champagne, N. Markova, V. Enchev and F. Castet, J. Phys. Chem. A, 2007, 111, 9914-9923.
3. C.-G. Liu and X.-H. Guan, J. Phys. Chem. C, 2013, 117, 7776-7783.
4. R. Bersohn, Y. H. Pao and H. L. Frisch, J. Chem. Phys., 1966, 45, 3184-3198.
5. F. Castet, E. Bogdan, A. Plaquet, L. Ducasse, B. Champagne and V. Rodriguez, J. Chem. Phys., 2012, 136, 024506.