### **Supplementary Information**

# Tuning of Second-Order Nonlinear Optical Properties Based on [2.2]paracyclophanes Isomer: the Relative Configuration and Polarizable Environment

Jin-Ting Ye,<sup>\*,†</sup> Jing-Hai Liu,<sup>†,‡</sup> Qiang Zhang,<sup>†</sup> Yong-Qing Qiu,<sup>§</sup> Li-Hui Wang<sup>†</sup>

<sup>†</sup>College of Chemistry and Materials Science, Inner Mongolia University for the Nationalities, Tongliao, 028000, China

 <sup>‡</sup> Inner Mongolia Key Laboratory of Carbon Nanomaterials Nano Innovation Institute (NII), Inner Mongolia University for the Nationalities, Tongliao, 028000, China
<sup>§</sup> Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China

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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 erf (x) <sup>1</sup> as following formula:

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

The range-separation parameter  $\omega$  represents the inverse of the distance at which the exchange changes from DFT-like to HF-like. In exact Kohn–Sham (KS) theory <sup>2</sup>, the negative HOMO energy –  $\varepsilon_{\rm H}(N)$  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:

$$J = \left| \varepsilon_{\rm H}(N) + IP(N) \right| \tag{2}$$

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

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

The above equation simultaneously applies the IP criterion for both neutral (*N*) and anion (*N* + 1) systems. In addition, the IP, electron affinity (EA) and exciton binding energy ( $E_b$ ) <sup>3</sup> were studied at same level. The calculations of vertical excitation energies of the lowest singlet ( $E_o(S_1)$ ) and triplet ( $E_o(T_1)$ ) excited states and the vertical singlet-triplet gap ( $\Delta E_{ST} = E_o(S_1) - E_o(T_1)$ ) have been calculated using the LR-TDDFT <sup>4</sup> with Tamm-Dancoff approximation (TDA) <sup>5-6</sup>.

In order to clarify the effect of the surrounding environment (such as "crystals") on the molecular photophysical properties, the polarizable continuum model (PCM)-tuned RS functional approach was used to simulate the solvent effect <sup>7-8</sup>, where the default integral equation formalism variant polarizable continuum model (IEFPCM) was imported by adding the "scrf(pcm, read)" keyword and defining the magnitude of the dielectric constant  $\varepsilon$ . The PCM description can experimentally determined parameters which reflect the response of the environments in their respective state (liquid or solid) due to it is based on these macroscopic, which can not only describe polarization effects in solution, but in general for any isotropic environment including amorphous thin films <sup>9</sup>. The  $\varepsilon$  of a molecular crystal or thin-film was evaluated via the Clausius– Mossotti relation <sup>10-11</sup>, which reads:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{\alpha}{V} \tag{4}$$

where V is the volume occupied by a single molecule, and  $\alpha$  term denotes the isotropic component of the molecular polarizability.

**Table S1.** Calculated the polarizabilities (Bohr<sup>3</sup>), volume (Bohr<sup>3</sup>) and dielectric constant  $\varepsilon$  simulated the solid thin-film environment for all molecules at the  $\omega$ B97XD/6-31G(d,p) level

Compound	α	V	З
cis-TPA-BZ	422.7	4627.6	2.8
trans-TPA-BZ	434.1	4641.3	2.9
cis-TPA-TRZ	610.5	6244.9	3.1
trans-TPA-TRZ	637.2	6262.9	3.3
cis-PhCz-BZ	420.8	4538.2	2.9
trans-PhCz-BZ	432.5	4549.4	3.0
cis-PhCz-TRZ	604.8	6140.4	3.1
trans-PhCz-TRZ	633.3	6174.5	3.3

	level.		
Compound	НОМО	LUMO	$E_{gap}$
cis-TPA-BZ	-6.69	0.19	6.89
trans-TPA-BZ	-6.77	0.19	6.96
cis-TPA-TRZ	-6.77	-0.11	6.67
trans-TPA-TRZ	-6.77	-0.13	6.64
cis-PhCz-BZ	-7.14	0.14	7.28
trans-PhCz-BZ	-7.19	0.11	7.30
cis-PhCz-TRZ	-7.23	-0.06	7.17
trans-PhCz-TRZ	-7.18	-0.22	6.96

**Table S2.** Calculated the HOMO, LUMO and  $E_{gap}$  values at the  $\omega$ B97XD/6-31G(d,p)

**Table S3.** The optimally tuned  $\omega$ , the  $\alpha$ ,  $\langle R^2 \rangle$  (×10<sup>3</sup> a.u.), individual components of first hyperpolarizabilities and total first hyperpolarizabilities (×10<sup>-30</sup> esu) of all studied compounds computed at  $\omega$ B97XD\* level with 6-31+G(d,p) basis set in gas and solid phases.

Compound	$^{a}\omega$	$\omega^d$	<r<sup>2&gt;</r<sup>	α	$\beta_{\mathrm{x}}$	$eta_{ ext{y}}$	$\beta_{z}$	${}^aeta_{\mathrm{tot}}$	${}^{b}\beta_{\mathrm{tot}}$
cis-TPA-BZ	0.135	0.030	23.0	7.1	-6.6	-0.7	-3.7	7.6	19.6
trans-TPA-BZ	0.138	0.028	32.8	7.3	-7.4	-0.5	-4.7	8.8	21.6
cis-TPA-TRZ	0.120	0.020	44.3	10.2	4.6	-3.3	-6.5	8.6	24.0
trans-TPA-TRZ	0.140	0.019	86.0	10.6	-35.7	8.0	-15.5	39.7	84.2
cis-PhCz-BZ	0.141	0.029	23.2	7.0	-3.0	-0.1	-1.5	3.3	8.2
trans-PhCz-BZ	0.145	0.027	33.7	7.2	-3.0	-0.6	-2.8	4.1	10.1
cis-PhCz-TRZ	0.135	0.022	43.7	10.1	7.9	-2.9	-1.3	8.5	26.7
trans-PhCz-TRZ	0.132	0.019	85.3	10.6	-26.0	3.3	12.2	28.9	58.8

The calculated  $\omega$  values in the <sup>a</sup>gas and <sup>b</sup>solid-state phases.



Figure S1. The total first hyperpolarizabilities ( $\times 10^{-30}$  esu) values of *trans*-TPA-TRZ as a function of the basis set in gas phase.



## Cis-TPA-Bz

Trans-TPA-Bz

Figure S2. The unit sphere representations of the Hyper-Rayleigh first hyperpolarizabilities tensor of *cis*-TPA-Bz and *trans*-TPA-Bz as calculated at the ωB97XD\* level of approximation (USR factor of 0.0008)

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