Supporting Information

Constructing Mixing π-Conjugated Bridge: A Simple and Effective Approach to Realize the Large First Hyperpolarizability in Carbon Nanotube-Based Systems

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Section I

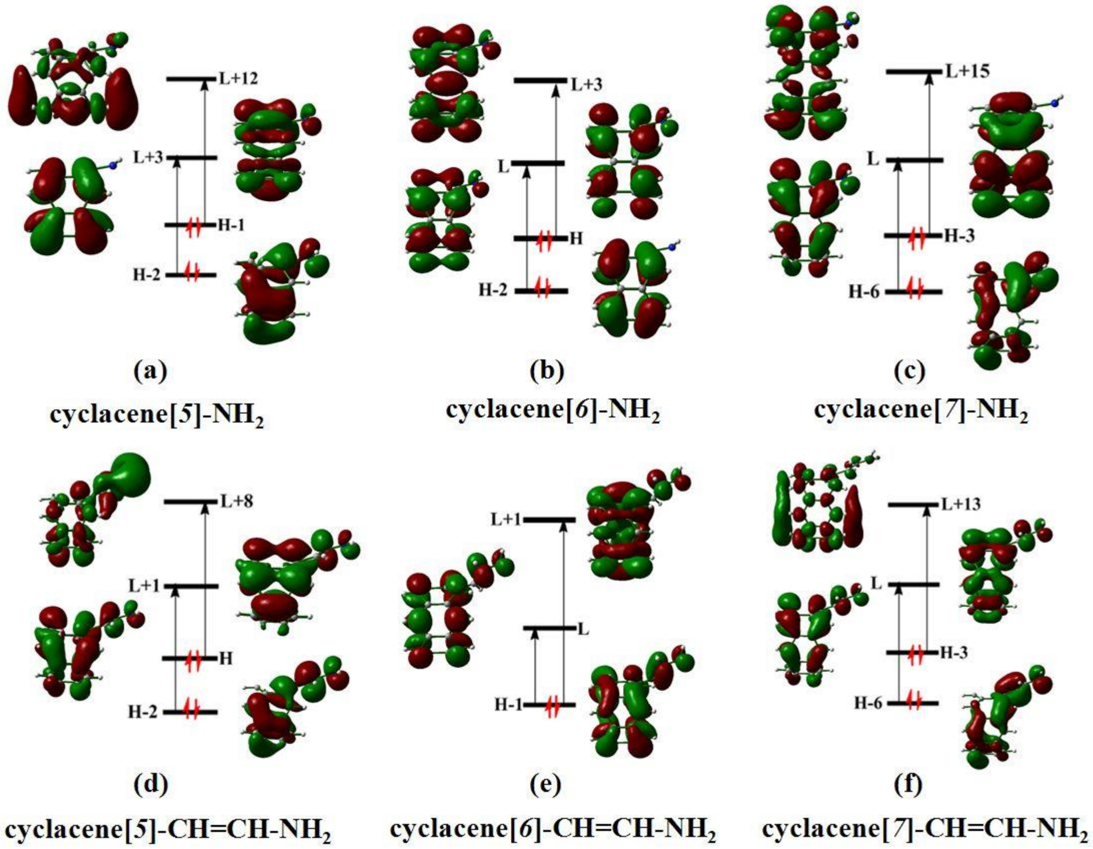

Figure S1. The crucial transition states of cyclacene[n] (n = 5, 6 and 7) decorated by –NH_2 and –CH=CH–NH_2 groups.

Section II

In this work, the measurable hyper-Rayleigh scattering (HRS) first hyperpolarizabilities of the related systems were computed according to the following expression:[1,2]

$$\beta_{HRS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{XZZ}^2 \rangle} \tag{1}$$

where the $\langle \beta_{ZZZ}^2 \rangle$ and $\langle \beta_{XZZ}^2 \rangle$ correspond to the orientational averages of the β tensor, and are presented as follows (without assuming Kleinman's conditions):

$$\begin{aligned}
\langle \beta_{ZZZ}^2 \rangle = {} & \frac{1}{7}\sum_{\varsigma}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}^2 + \frac{4}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\eta}^2 + \frac{2}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}\beta_{\varsigma\eta\eta} + \\
& \frac{4}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\eta\varsigma\varsigma}\beta_{\varsigma\varsigma\eta} + \frac{4}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}\beta_{\eta\eta\varsigma} + \frac{1}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\eta\varsigma\varsigma}^2 \\
& + \frac{4}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\varsigma\eta}\beta_{\eta\xi\xi} + \frac{1}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\eta\varsigma\varsigma}\beta_{\eta\xi\xi} \\
& + \frac{4}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\varsigma\eta}\beta_{\xi\xi\eta} + \frac{2}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\eta\xi}^2 + \frac{4}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\eta\xi}\beta_{\eta\xi\varsigma}
\end{aligned} \tag{2}$$

$$\begin{aligned}
\langle \beta_{XZZ}^2 \rangle = {} & \frac{1}{35}\sum_{\varsigma}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}^2 + \frac{4}{105}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}\beta_{\varsigma\eta\eta} - \frac{2}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\varsigma}\beta_{\eta\eta\varsigma} \\
& + \frac{8}{105}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\eta}^2 + \frac{3}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\eta\eta}^2 - \frac{2}{35}\sum_{\varsigma\neq\eta}^{x,y,z} \beta_{\varsigma\varsigma\eta}\beta_{\eta\varsigma\varsigma} \\
& + \frac{1}{35}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\eta\eta}\beta_{\varsigma\xi\xi} - \frac{2}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\varsigma\xi}\beta_{\eta\eta\xi} - \frac{2}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\varsigma\eta}\beta_{\eta\xi\xi} \\
& + \frac{2}{35}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\eta\xi}^2 - \frac{2}{105}\sum_{\varsigma\neq\eta\neq\xi}^{x,y,z} \beta_{\varsigma\eta\xi}\beta_{\eta\varsigma\xi}
\end{aligned} \tag{3}$$

Here, the correlative components of static fist hyperpolarizability tensor in these equations are obtained by using the coupled perturbed Hartree-Fock (CPHF) method with the basis set 6-31G(d). All the computations were carried out by using the GAUSSIAN 09 program package.

As shown in the following Figures **S2**, **S3** and **S4**, it was found that those findings based on the computed results of β_0 in the text can also be supported by their corresponding computed β_{HRS} results.

References:

(1) R. Bersohn, Y. H. Pao, H. L. Frisch, *J Chem Phys* 1966, **45**, 3184.

(2) S. N. Labidi, M. B. Kanoun, M. D. Wergifosse, B. Champagne, *Inter. J. of Quantum Chem.* 2011, **111**, 1583.

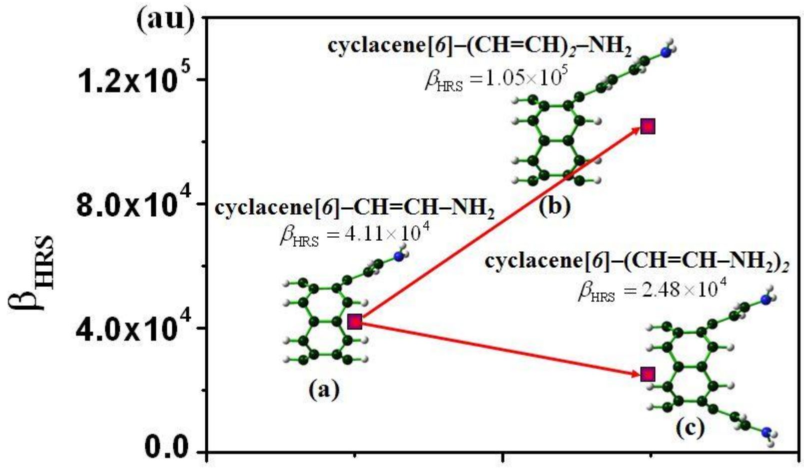

Figure S2. The HRS first hyperpolarizabilities (β_{HRS}) of **(a)** cyclacene[*6*]–CH=CH–NH_2, **(b)** cyclacene[*6*]–$(CH{=}CH)_2$–NH_2 and **(c)** cyclacene[*6*]–$(CH{=}CH{-}NH_2)_2$.

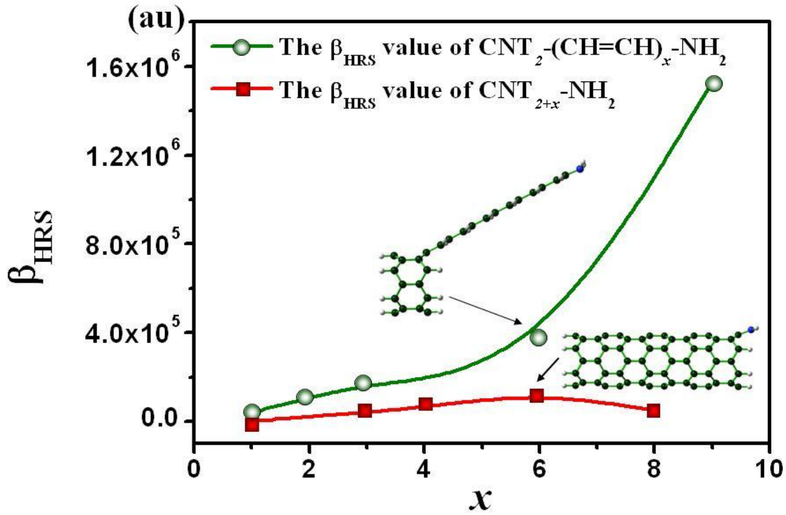

Figure S3. The relationship of the HRS first hyperpolarizability (β_{HRS}) versus *x* values for both CNT_2–$(CH{=}CH)_x$–NH_2 (x = 1, 2, 3, 6 and 9) and CNT_{2+x}–NH_2 (x = 1, 3, 4, 6 and 8) series.

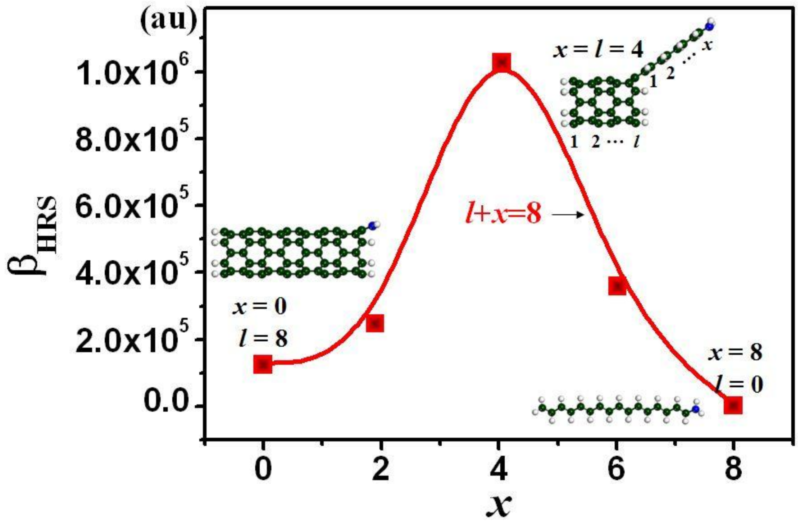

Figure S4. Dependence of the HRS first hyperpolarizability (β_{HRS}) value on the length of the –(CH=CH)$_x$– chain (x) in CNT$_l$–(CH=CH)$_x$–NH$_2$ ($l + x = 8$, x = 0, 2, 4, 6 and 8).