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# Supporting Information

## Tuning the edge states in X-type carbon based molecules for application in nonlinear optics

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**Supporting Information list:**

**Figure S1** The electronic spectra of experimentally synthesized molecule DHR with (a) experiment (black line)[1] and the simulated absorptions due to $S_0$-$S_1$ (sky-blue line) and $S_0$-$S_2$ (green line) transitions[1] and (b) predicted with ZINDO.

**Figure S2** The molecular orbitals associated with the major electron excitations in (a) $X_4$-CO, and (b) $X_4$-CO-NA.

**Figure S3** Structures of X-armchair graphene nanoribbon with azulenes, aniline, formoxime and tert-butylamine.

**Figure S4** Predicted the static first hyperpolarizabilities $<\beta_0>$ (in $10^{-30}$ esu) of $X_1$-H6, $X_4$-CO, $X_4$-CO-NA, and $X_4$-CO-AN from sum-over-states (SOS) model and coupled perturbed Kohn-Sham model (CPKS) at PBE0/6-31G(d,p).

**Figure S5** Structures and frontier molecular orbitals of pure and substituted azulene. The red numbers are bond length in Angstroms.

**Figure S6.** Electronic spectra of azulene and substituted azulenes predicted by ZINDO method and CAM-B3LYP/6-31G++(d,p).

**Figure S7.** (a) Electronic spectra of azulene predicted by ZINDO method and CAM-B3LYP/6-31G++(d,p); (b) Electronic spectra of azulene and naphthalene measured in gas phase.[S2,S3]

**Table S1** C-N bond distances (Å) in $X_4$-CO-NA (AN), substituted azulene, aniline, formoxime and tert-butylamine.

**Table S2** Major electronic excitations with transition nature in X-type molecules, azulene and substituted azulene

**Table S3** Predicted major $\beta_{ijk}$ [i, j, k∈(x, y, z)] ($\times 10^{-30}$ esu) of $X_4$-CO-NA and $X_4$-CO-AN and the related molecular properties with important contributions to the $\beta_{ijk}$ according to the SOS model.

**Table S4** The electronic properties and static first hyperpolarizability ($<\beta_0>$), the energy gaps ($E_{gap}$) between the highest occupied molecular orbital ($E_{HOMO}$) and the lowest unoccupied molecular orbital ($E_{LUMO}$) and the lowest vibrational frequency (LVF) of are closed-shell singlet predicted with PBE0/6-31G(d,p). The relative electronic energy differences ($\Delta E_{OS-CS}$ and $\Delta E_{T-CS}$) between open-shell singlet (OS) or triplet (T) and closed-shell singlet (CS) (CS is taken as the reference), and spin contamination of open-shell singlet ($<S^2>$) predicted at UPBE0/6-31G(d,p) level.

**Table S5** Predicted major $\beta_{ijk}$ [i, j, k∈(x, y, z)] ($\times 10^{-30}$ esu) of azulene and $NO_2$ substituted azulene and the related molecular properties with important contributions to the $\beta_{ijk}$ according to the SOS model.

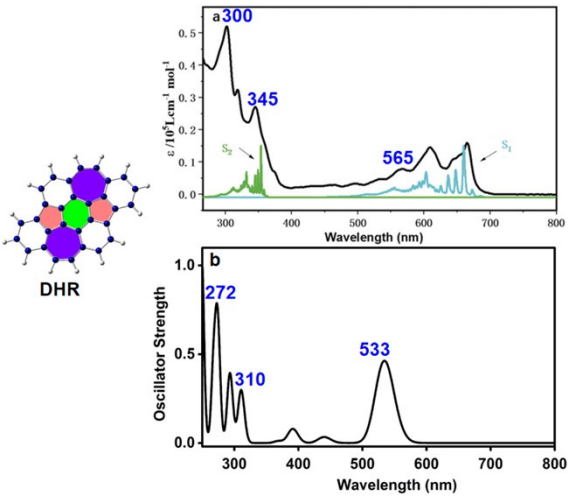
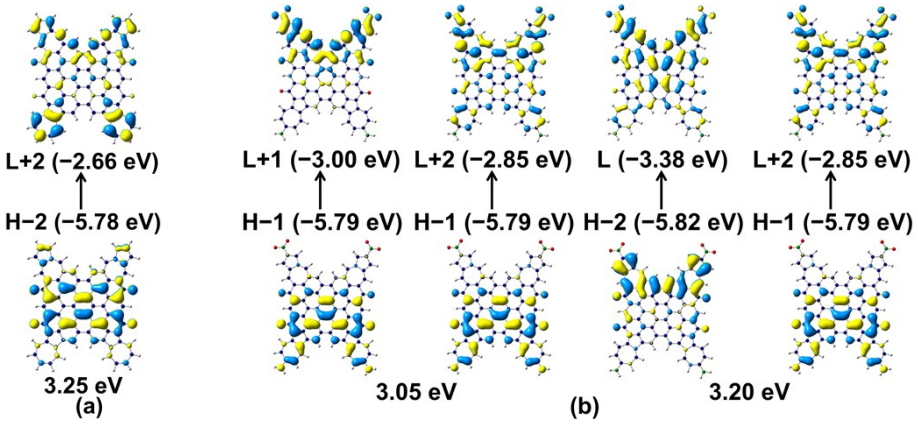



**Figure S1** The electronic spectra of experimentally synthesized molecule DHR with (a) experiment (black line)[S1] and the simulated absorptions due to $S_0$-$S_1$ (sky-blue line) and $S_0$-$S_2$ (green line) transitions[S1] and (b) predicted with ZINDO.

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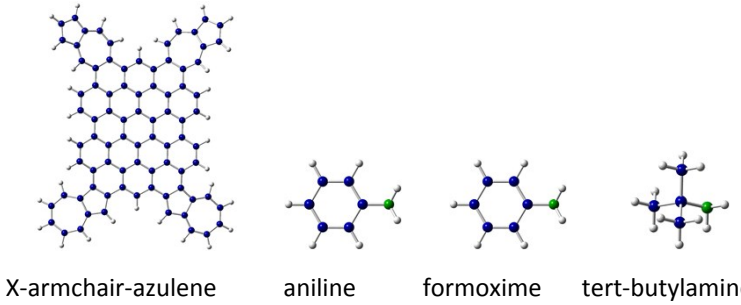


**Figure S3** Structures of X-armchair graphene nanoribbon with azulenes, aniline, formoxime and tert-butylamine.

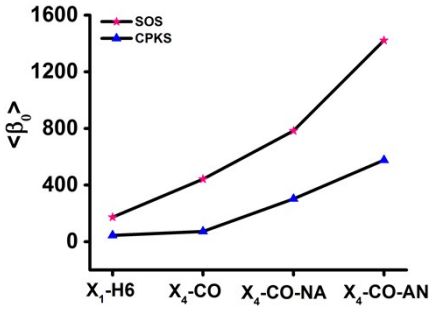


**Figure S4** Predicted the static first hyperpolarizabilities <$\beta_0$> (in $10^{-30}$ esu) of $X_1$-H6, $X_4$-CO, $X_4$-CO-NA, and $X_4$-CO-AN from sum-over-states (SOS) model and coupled perturbed Kohn-Sham model (CPKS) at PBE0/6-31G(d,p).

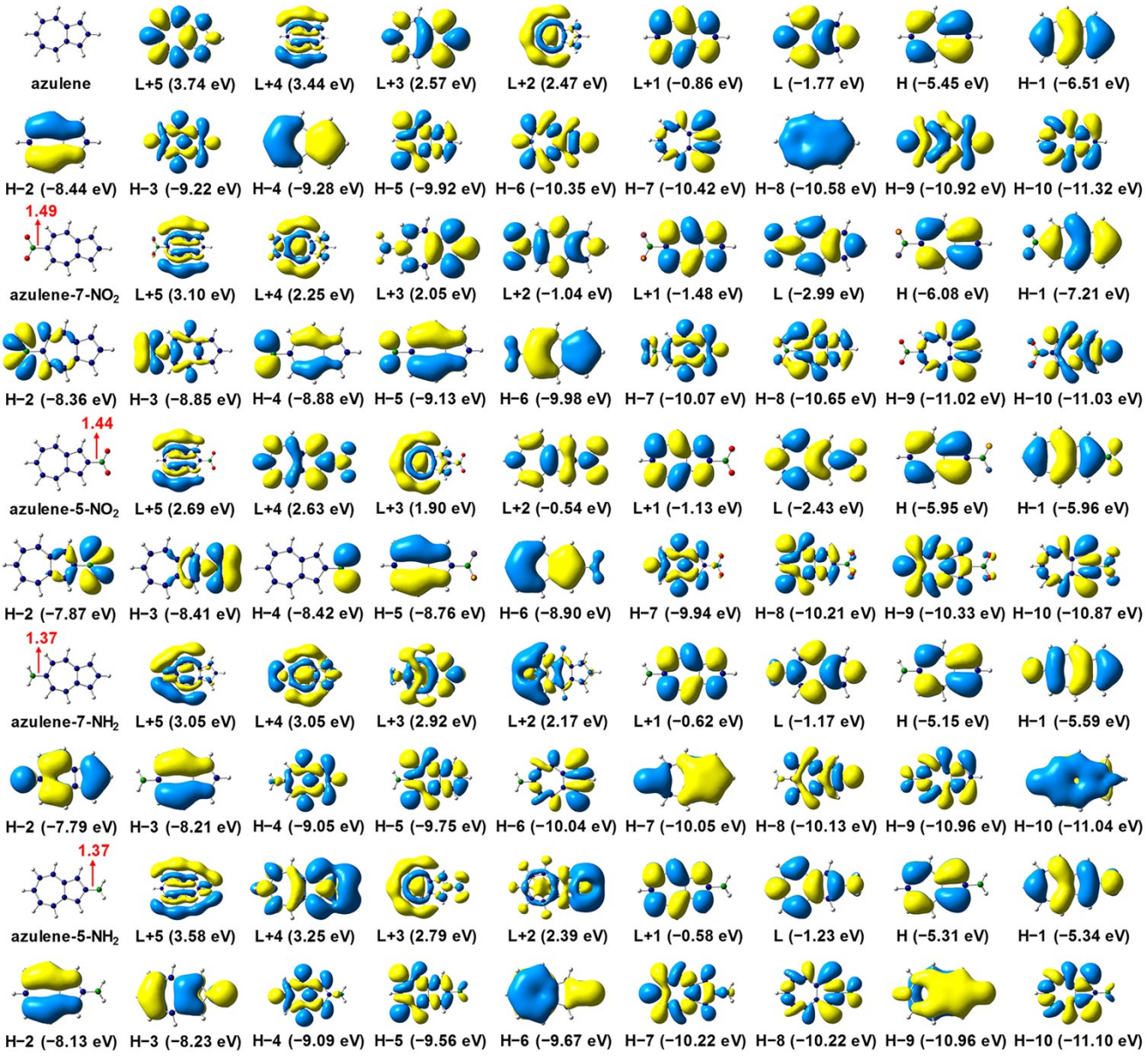


**Figure S5** Structures and frontier molecular orbitals of pure and substituted azulene. The red numbers are bond length in Angstroms.

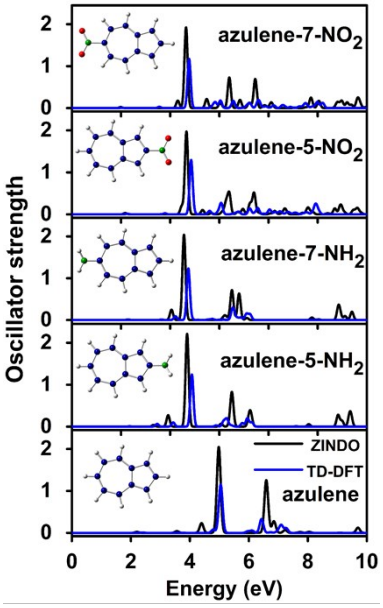


**Figure S6.** Electronic spectra of azulene and substituted azulenes predicted by ZINDO method and CAM-B3LYP/6-31G++(d,p).

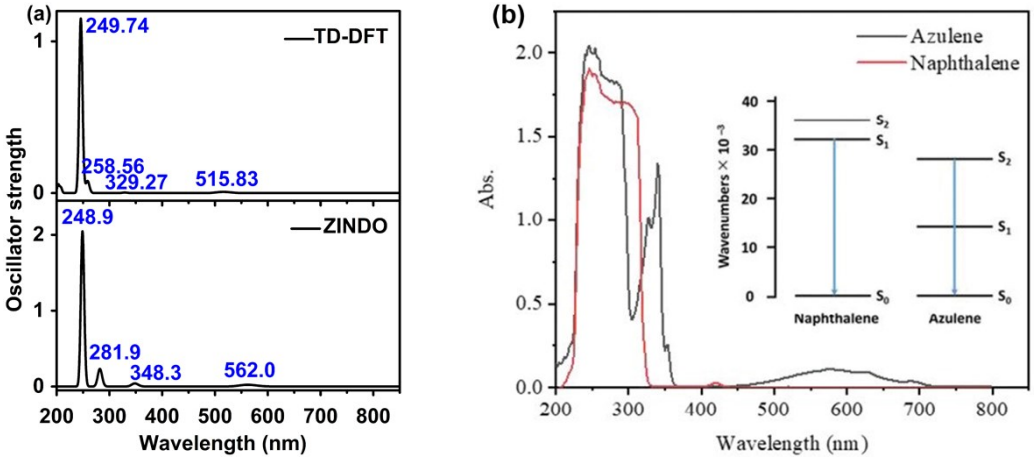


**Figure S7.** (a) Electronic spectra of azulene predicted by ZINDO method and CAM-B3LYP/6-31++G(d,p); (b) Electronic spectra of azulene and naphthalene measured in gas phase.[S2,S3]

**Table S1** C-N bond distances (Å) in $X_4$-CO-NA (AN), substituted azulene, aniline, formoxime and tert-butylamine. $C_5$–N is bond distance between the carbon atom of pentagon and the nitrogen atom of $NH_2$ or $NO_2$; $C_7$–N is bond distance between the carbon atom of heptagon and the nitrogen atom of $NH_2$ or $NO_2$. C–N is carbon-nitrogen bond distance of aniline, formoxime or tert-butylamine.

| Compound | $C_5$–N | $C_7$–N | C–N |
|---|---|---|---|
| $X_4$-CO-NA | 1.44 | 1.36 | |
| $X_4$-CO-AN | 1.36 | 1.49 | |
| azulene-5-$NH_2$ | 1.37 | | |
| azulene-5-$NO_2$ | 1.44 | | |
| azulene-7-$NH_2$ | | 1.37 | |
| azulene-7-$NO_2$ | | 1.49 | |
| aniline | | | 1.39 |
| formoxime | | | 1.27 |
| tert-butylamine | | | 1.47 |

**Table S2** Major electronic excitations with transition nature in X-type molecules, azulene and substituted azulene (*f* is the oscillator strength in arbitrary unit, E is the transition energy in eV (nm) unit, Contribution value to $<\beta_0>$ in $10^{-30}$ esu unit).

| Compounds | *f* | E | Transition | Major contributions to $<\beta_0>$ | Contribution value to $<\beta_0>$ |
|---|---|---|---|---|---|
| $X_1$-H6 ($C_{78}H_{36}$) | 0.1866 | 1.76 | $S_0 \rightarrow S_1$ | H→L (27.48%)<br>H→L+1 (56.14%) | −61.41 |
| | 1.2202 | 1.93 | $S_0 \rightarrow S_2$ | H→L (57.97%)<br>H→L+1 (20.76%) | 121.01 |
| | 0.2346 | 2.34 | $S_0 \rightarrow S_6$ | H→L+2 (56.39%) | −111.57 |
| | 0.4577 | 2.55 | $S_0 \rightarrow S_{11}$ | H→L+6 (37.52%)<br>H−1→L (15.82%) | −196.72 |
| $X_4$-CO ($C_{78}H_{26}O_4$) | 0.2418 | 2.08 | $S_0 \rightarrow S_1$ | H−1→L+3 (11.79%)<br>H→L (44.59%)<br>H→L+3 (11.77%) | 62.60 |
| | 0.6248 | 2.57 | $S_0 \rightarrow S_5$ | H−3→L+6 (10.95%)<br>H→L (20.31%)<br>H→L+5 (12.05%) | −45.16 |
| | 0.7172 | 2.90 | $S_0 \rightarrow S_9$ | H−5→L (23.12%)<br>H−3→L+1 (12.32%)<br>H−2→L+4 (16.42%) | 52.66 |
| | 2.5305 | 2.92 | $S_0 \rightarrow S_{10}$ | H−2→L (37.14%)<br>H−1→L+1 (10.91%)<br>H→L+4 (12.73%) | 23.44 |
| | 1.6253 | 3.25 | $S_0 \rightarrow S_{17}$ | H−2→L+2 (26.92%) | 161.76 |
| $X_4$-CO-NA ($C_{78}H_{26}N_4O_8$) | 0.4970 | 2.08 | $S_0 \rightarrow S_1$ | H−2→L (10.37%)<br>H→L (47.18%) | −61.72 |
| | 0.7411 | 2.50 | $S_0 \rightarrow S_6$ | H→L (24.81%)<br>H→L+6 (23.49%) | −139.76 |
| | 2.1567 | 2.91 | $S_0 \rightarrow S_{12}$ | H−2→L+1 (10.04%)<br>H−1→L (19.08%)<br>H→L+4 (15.53%) | −32.71 |
| | 1.2614 | 3.05 | $S_0 \rightarrow S_{13}$ | H−1→L+2 (35.77%)<br>H−1→L+1 (10.82%) | −205.66 |
| | 1.6595 | 3.20 | $S_0 \rightarrow S_{16}$ | H−2→L (17.77%)<br>H−1→L+2 (15.70%) | −16.98 |
| | 0.7776 | 3.37 | $S_0 \rightarrow S_{22}$ | H→L+3 (25.80%)<br>H−1→L+1 (10.19%) | −143.72 |
| | 0.3560 | 4.02 | $S_0 \rightarrow S_{46}$ | H−7→L (11.04%)<br>H−3→L+2 (10.11%) | −39.26 |
| $X_4$-CO-AN ($C_{78}H_{26}N_4O_8$) | 0.0248 | 1.92 | $S_0 \rightarrow S_1$ | H−6→L+1 (10.72%)<br>H−2→L (18.04%)<br>H→L (31.69%) | −17.59 |
| | 0.4417 | 2.24 | $S_0 \rightarrow S_3$ | H→L (16.81%)<br>H−2→L+2 (25.00%) | −46.74 |
| | 2.0427 | 2.91 | $S_0 \rightarrow S_{12}$ | H−2→L+3 (13.74%) | −89.95 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | H−1→L (24.81%)<br>H→L+4 (10.01%) | |
| | 2.7777 | 3.05 | $S_0 \rightarrow S_{13}$ | H−1→L+1 (27.78%)<br>H−1→L+4 (10.61%) | −355.73 |
| | 0.6405 | 3.11 | $S_0 \rightarrow S_{17}$ | H−2→L+7 (10.60%)<br>H−2→L (14.69%) | −111.48 |
| | 0.2506 | 3.50 | $S_0 \rightarrow S_{30}$ | H−4→L (11.64%)<br>H−2→L (11.99%) | −57.20 |
| | 0.2431 | 3.82 | $S_0 \rightarrow S_{40}$ | H−2→L+2 (20.63%) | −55.27 |
| | 0.5087 | 3.89 | $S_0 \rightarrow S_{42}$ | H→L+9 (10.17%) | −18.05 |
| | 0.4451 | 4.04 | $S_0 \rightarrow S_{49}$ | H→L+7 (11.13%) | −34.96 |
| | 0.2919 | 4.28 | $S_0 \rightarrow S_{62}$ | H−3→L+2 (12.47%) | −15.79 |
| | 0.0975 | 4.29 | $S_0 \rightarrow S_{63}$ | H−10→L (10.73%) | −11.56 |
| | 0.1636 | 4.33 | $S_0 \rightarrow S_{67}$ | H−3→L+1 (24.21%) | −26.56 |
| | 0.6577 | 4.48 | $S_0 \rightarrow S_{76}$ | H−4→L+2 (11.98%) | −113.70 |
| | 0.2412 | 4.58 | $S_0 \rightarrow S_{83}$ | H−5→L+3 (13.45%) | −15.78 |
| azulene ($C_{10}H_8$) | 2.0474 | 4.98 | $S_0 \rightarrow S_4$ | H−1→L (63.28%)<br>H→L+1 (34.05%) | 52.86 |
| azulene-5-$NO_2$ ($C_{10}H_7NO_2$) | 0.0316 | 2.17 | $S_0 \rightarrow S_1$ | H→L (90.54%) | 3.63 |
| | 0.1904 | 4.47 | $S_0 \rightarrow S_6$ | H−1→L (74.15%) | 1.17 |
| | 1.9718 | 4.66 | $S_0 \rightarrow S_7$ | H−1→L (39.83%)<br>H→L+1 (35.87%) | −1.86 |
| | 0.1025 | 5.32 | $S_0 \rightarrow S_8$ | H−1→L+2 (84.14%) | −2.64 |
| | 0.2571 | 6.28 | $S_0 \rightarrow S_{17}$ | H−5→L (33.28%)<br>H−4→L (22.94%)<br>H→L+3 (28.81%) | 1.61 |
| | 0.4897 | 6.40 | $S_0 \rightarrow S_{18}$ | H−4→L (50.98%)<br>H→L+4 (74.29%) | 2.42 |
| | 0.4872 | 7.42 | $S_0 \rightarrow S_{33}$ | H−4→L+2 (78.21%)<br>H−1→L+7 (12.07%) | 1.18 |
| | 0.1096 | 9.58 | $S_0 \rightarrow S_{59}$ | H−2→L+6 (90.03%) | 1.33 |
| azulene-5-$NH_2$ ($C_{10}H_9N$) | 2.2084 | 4.69 | $S_0 \rightarrow S_4$ | H−1→L (39.83%)<br>H→L+1 (57.81%) | 19.06 |
| azulene-7-$NO_2$ ($C_{10}H_7NO_2$) | 1.9229 | 4.65 | $S_0 \rightarrow S_7$ | H−1→L (51.32%)<br>H→L+1 (38.95%) | −106.69 |
| azulene-7-$NH_2$ ($C_{10}H_9N$) | 2.0388 | 4.56 | $S_0 \rightarrow S_4$ | H−1→L (49.35%)<br>H→L+1 (43.30%) | 42.02 |

**Table S3** Predicted major $\beta_{ijk}$ [i, j, k∈(x, y, z)] (×$10^{-30}$ esu) of $X_4$-CO-NA and $X_4$-CO-AN and the related molecular properties with important contributions to the $\beta_{ijk}$ according to the SOS model. [m=0 is the ground state; m>0 is the mth excited state].

| Structures (<$\beta_0$>) | $\beta_{zzz}$ | $\beta_{xxx}$ | $\beta_{yyx}$ | State [$S_m$(m≥0)] | Excitation energy | State dipole moment | | | | Transition dipole moment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | X | Y | Z | tot | X | Y | Z | tot |
| | | | | $S_0$ | | 0.00 | 0.00 | 30.16 | 30.16 | | | | |
| | −61.72 | 0.00 | 0.00 | $S_1$ [$S_0 \rightarrow S_1$] | 2.08 | 0.00 | 0.00 | 31.98 | 31.98 | 0.00 | 0.00 | −7.93 | 7.93 |
| $X_4$-CO-NA (−783.23) | −139.76 | 0.00 | 0.00 | $S_6$ [$S_0 \rightarrow S_6$] | 2.50 | 0.00 | 0.00 | 34.96 | 34.96 | 0.00 | 0.00 | −8.83 | 8.83 |
| | −205.66 | 0.00 | 0.00 | $S_{13}$ [$S_0 \rightarrow S_{13}$] | 3.05 | 0.00 | 0.00 | 37.70 | 37.70 | 0.00 | 0.00 | 10.43 | 10.43 |
| | −143.72 | 0.00 | 0.00 | $S_{22}$ [$S_0 \rightarrow S_{22}$] | 3.37 | 0.00 | 0.00 | 41.67 | 41.67 | 0.00 | 0.00 | 7.79 | 7.79 |
| | −39.26 | 0.00 | 0.00 | $S_{46}$ [$S_0 \rightarrow S_{46}$] | 4.02 | 0.00 | 0.00 | 41.82 | 41.82 | 0.00 | 0.00 | 4.83 | 4.83 |
| | | | | $S_0$ | | 6.59 | 0.00 | 0.00 | 6.59 | | | | |
| | 0.00 | 0.00 | −89.95 | $S_{12}$ [$S_0 \rightarrow S_{12}$] | 2.91 | 11.87 | 0.00 | 0.00 | 11.87 | 0.00 | 13.60 | 0.15 | 13.62 |
| | 0.00 | −355.73 | 0.00 | $S_{13}$ [$S_0 \rightarrow S_{13}$] | 3.05 | 12.52 | 0.00 | 0.01 | 12.52 | −15.48 | 0.00 | 0.00 | 15.48 |
| | 0.00 | −111.48 | 0.00 | $S_{17}$ [$S_0 \rightarrow S_{17}$] | 3.11 | 15.56 | 0.00 | 0.06 | 15.56 | 7.16 | 0.00 | 0.00 | 7.16 |
| | 0.00 | −54.08 | 0.00 | $S_{30}$ [$S_0 \rightarrow S_{30}$] | 3.50 | 22.48 | 0.00 | 0.01 | 22.48 | 4.34 | 0.00 | 0.00 | 4.34 |
| | −0.56 | −55.27 | 0.00 | $S_{40}$ [$S_0 \rightarrow S_{40}$] | 3.82 | 27.19 | 0.00 | 0.01 | 27.19 | −4.09 | 0.00 | 0.00 | 4.09 |
| $X_4$-CO-AN (−1421.98) | −0.10 | 0.00 | −18.04 | $S_{42}$ [$S_0 \rightarrow S_{42}$] | 3.89 | 16.80 | 0.00 | 0.01 | 16.80 | 0.00 | 5.86 | 0.13 | 5.88 |
| | 0.00 | −34.96 | 0.00 | $S_{49}$ [$S_0 \rightarrow S_{49}$] | 4.04 | 15.02 | 0.00 | 0.01 | 15.02 | 5.39 | 0.00 | 0.00 | 5.39 |
| | 0.00 | 0.00 | −15.77 | $S_{62}$ [$S_0 \rightarrow S_{62}$] | 4.28 | 27.21 | 0.00 | 0.01 | 27.21 | 0.00 | 4.24 | −0.17 | 4.27 |
| | 0.00 | −11.56 | 0.00 | $S_{63}$ [$S_0 \rightarrow S_{63}$] | 4.29 | 21.79 | 0.00 | 0.01 | 21.79 | −2.45 | 0.00 | 0.00 | 2.45 |
| | 0.00 | −26.56 | 0.00 | $S_{67}$ [$S_0 \rightarrow S_{67}$] | 4.33 | 28.07 | 0.00 | 0.00 | 28.07 | −3.15 | 0.00 | 0.00 | 3.15 |
| | 0.00 | −113.70 | 0.00 | $S_{76}$ [$S_0 \rightarrow S_{76}$] | 4.48 | 31.92 | 0.00 | 0.01 | 31.92 | −6.21 | 0.00 | 0.00 | 6.21 |
| | 0.00 | −15.78 | 0.00 | $S_{83}$ [$S_0 \rightarrow S_{83}$] | 4.58 | 16.83 | 0.00 | 0.01 | 16.83 | −3.72 | 0.00 | 0.00 | 3.72 |

(1) $X_4$-CO-NA:

$$\beta_{ZZZ}[S_0 \rightarrow S_1]=6\times\frac{-7.93\times(31.98-30.16)\times 7.93}{2.08^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-61.84\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_6]=6\times\frac{-8.83\times(34.96-30.16)\times 8.83}{2.50^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-139.99\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_{13}]=6\times\frac{10.43\times(37.70-30.16)\times(-10.43)}{3.05^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-206.14\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_{22}]=6\times\frac{7.79\times(41.67-30.16)\times(-7.79)}{3.37^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-143.79\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_{46}]=6\times\frac{4.83\times(41.82-30.16)\times(-4.83)}{4.02^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-39.35\times10^{-30}esu$$

(2) $X_4$-CO-AN:

$$\beta_{YYX}[S_0 \to S_{12}] = [2 \times \frac{13.60 \times (11.87 - 6.59) \times (-13.60)}{2.91^2} + 4 \times \frac{13.60 \times (0.00 - 0.00) \times (-13.60)}{2.91^2}] \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu$$

$$= -89.87 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{13}] = 6 \times \frac{(-15.48) \times (12.52 - 6.59) \times 15.48}{3.05^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = 357.13 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{17}] = 6 \times \frac{7.16 \times (15.56 - 6.59) \times (-7.16)}{3.11^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -111.15 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{30}] = 6 \times \frac{4.34 \times (22.48 - 6.59) \times (-4.34)}{3.50^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -57.12 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{40}] = 6 \times \frac{(-4.09) \times (27.19 - 6.59) \times 4.09}{3.82^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -55.21 \times 10^{-30} esu$$

$$\beta_{YYX}[S_0 \to S_{42}] = [2 \times \frac{5.86 \times (16.80 - 6.59) \times (-5.86)}{3.89^2} + 4 \times \frac{5.86 \times (0.00 - 0.00) \times (-5.86)}{3.89^2}] \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu$$

$$= -18.06 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{49}] = 6 \times \frac{5.39 \times (15.02 - 6.59) \times (-5.39)}{4.04^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -35.08 \times 10^{-30} esu$$

$$\beta_{YYX}[S_0 \to S_{62}] = [2 \times \frac{4.24 \times (27.21 - 6.59) \times (-4.24)}{4.28^2} + 4 \times \frac{0.00 \times (0.00 - 0.00) \times 0.00}{4.28^2}] \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu$$

$$= -15.77 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{63}] = 6 \times \frac{-2.45 \times (21.79 - 6.59) \times 2.45}{4.29^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -11.59 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{67}] = 6 \times \frac{-3.15 \times (28.07 - 6.59) \times 3.15}{4.33^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -26.58 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{76}] = 6 \times \frac{-6.21 \times (31.92 - 6.59) \times 6.21}{4.48^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -113.79 \times 10^{-30} esu$$

$$\beta_{XXX}[S_0 \to S_{67}] = 6 \times \frac{-3.72 \times (16.83 - 6.59) \times 3.72}{4.58^2} \times \frac{(10^{-18})^3}{(1.602 \times 10^{-12})^2} esu = -15.79 \times 10^{-30} esu$$

**Table S4** The electronic properties and static first hyperpolarizability (<$\beta_0$>), the energy gaps ($E_{gap}$) between the highest occupied molecular orbital ($E_{HOMO}$) and the lowest unoccupied molecular orbital ($E_{LUMO}$) and the lowest vibrational frequency (LVF) of are closed-shell singlet predicted with PBE0/6-31G(d,p). The relative electronic energy differences ($\Delta E_{OS-CS}$ and $\Delta E_{T-CS}$) between open-shell singlet (OS) or triplet (T) and closed-shell singlet (CS) (CS is taken as the reference), and spin contamination of open-shell singlet (<$S^2$>) predicted at UPBE0/6-31G(d,p) level.

| Compound | $\Delta E_{OS-CS}$ (kcal/mol) | $\Delta E_{T-CS}$ (kcal/mol) | <$S^2$> | LVF /$cm^{-1}$ | $E_{HOMO}$/eV | $E_{LUMO}$/eV | $E_{gap}$/eV | $\beta_0$ ($\beta_0$/N) (×$10^{-30}$ esu) |
|---|---|---|---|---|---|---|---|---|
| DHR ($C_{30}H_{14}$) | −0.03 | 24.12 | 0.00 | 49.94 | −4.95 | −2.43 | 2.52 | * |
| X-armchair-azulene ($C_{82}H_{34}$) | 0.00 | 30.25 | 0.00 | 7.04 | −4.85 | −2.36 | 2.49 | −45.62 (−0.56) |
| azulene ($C_{10}H_8$) | 0.00 | 35.74 | 0.00 | 163.33 | −5.44 | −1.77 | 3.67 | 59.29 (5.93) |
| azulene-5-$NO_2$ ($C_{10}H_7NO_2$) | 0.00 | 33.74 | 0.00 | 60.82 | −6.19 | −2.84 | 3.35 | 8.40 (0.65) |
| azulene-5-$NH_2$ ($C_{10}H_9N$) | 0.00 | 41.25 | 0.00 | 117.00 | −5.31 | −1.23 | 4.08 | 22.34 (2.03) |
| azulene-7-$NO_2$ ($C_{10}H_7NO_2$) | 0.00 | 27.61 | 0.00 | 29.70 | −6.08 | −2.99 | 3.09 | −118.08 (−9.08) |
| azulene-7-$NH_2$ ($C_{10}H_9N$) | 0.00 | 42.56 | 0.00 | 106.93 | −5.15 | −1.17 | 3.98 | 41.31 (3.76) |

N is the number of heavy atoms. *: The <$\beta_0$> of this molecule is not discussed in this work.

**Table S5** Predicted major $\beta_{ijk}$ [i, j, k∈(x, y, z)] (×$10^{-30}$ esu) of azulene and $NO_2$ substituted azulene and the related molecular properties with important contributions to the $\beta_{ijk}$ according to the SOS model. [m=0 is the ground state; m>0 is the mth excited state].

| Structures (<$\beta_0$>) | $\beta_{zzz}$ | $\beta_{yyy}$ | $\beta_{yyz}$ | State [$S_m$(m≥0)] | Excitation energy | State dipole moment | | | | Transition dipole moment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | X | Y | Z | tot | X | Y | Z | tot |
| azulene | | | | $S_0$ | | 0.00 | 0.00 | −2.09 | 2.09 | | | | |
| | −52.86 | 0.00 | 0.00 | $S_4$ [$S_0 \rightarrow S_4$] | 4.98 | 0.00 | 0.00 | 3.10 | 3.10 | 0.00 | 0.00 | −10.40 | 10.40 |
| azulene-5-$NO_2$ | | | | $S_0$ | | 0.00 | 0.00 | −8.72 | 8.72 | | | | |
| | 0.00 | 0.00 | −4.65 | $S_1$ [$S_0 \rightarrow S_1$] | 2.17 | 0.00 | 0.00 | −4.76 | 4.76 | 0.00 | 1.96 | 0.00 | 1.96 |
| | 1.87 | 0.00 | 0.00 | $S_7$ [$S_0 \rightarrow S_7$] | 4.66 | 0.00 | 0.00 | −8.87 | 8.87 | 0.00 | 0.00 | −10.55 | 10.55 |
| | 2.64 | 0.00 | 0.00 | $S_8$ [$S_0 \rightarrow S_8$] | 5.32 | 0.00 | 0.00 | −14.69 | 14.69 | 0.00 | 0.00 | −2.25 | 2.25 |
| | 0.00 | 0.00 | −2.51 | $S_{18}$ [$S_0 \rightarrow S_{18}$] | 6.40 | 0.00 | 0.00 | −2.62 | 2.62 | 0.00 | 4.49 | 0.00 | 4.49 |
| azulene-7-$NO_2$ | | | | $S_0$ | | 0.00 | 0.00 | −4.15 | 4.15 | | | | |
| | 106.68 | 0.00 | 0.00 | $S_7$ [$S_0 \rightarrow S_7$] | 4.65 | 0.00 | 0.00 | −12.55 | 12.55 | 0.00 | 0.00 | −10.44 | 10.44 |

(1) azulene:

$$\beta_{ZZZ}[S_0 \rightarrow S_4]=6\times\frac{-10.40\times[3.10-(-2.09)]\times10.40}{4.98^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=-52.92\times10^{-30}esu$$

(2) azulene-5-$NO_2$:

$$\beta_{YYZ}[S_0 \rightarrow S_1]=[2\times\frac{1.96\times(0.00-0.00)\times(-1.96)}{2.17^2}+4\times\frac{1.96\times[-4.76-(-8.72)]\times(-1.96)}{2.17^2}]\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu$$

$$=-5.04\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_7]=6\times\frac{(-10.55)\times[-8.87-(-8.72)]\times10.55}{4.66^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=1.78\times10^{-30}esu$$

$$\beta_{ZZZ}[S_0 \rightarrow S_8]=6\times\frac{(-2.25)\times[-14.69-(-8.72)]\times2.25}{5.32^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=2.50\times10^{-30}esu$$

$$\beta_{YYZ}[S_0 \rightarrow S_{18}]=[2\times\frac{4.49\times[-2.62-(-8.72)]\times(-4.49)}{6.40^2}+4\times\frac{4.49\times(0.00-0.00)\times(-4.49)}{6.40^2}]\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu$$

$$=-2.34\times10^{-30}esu$$

(3) azulene-7-$NO_2$:

$$\beta_{ZZZ}[S_0 \rightarrow S_7]=6\times\frac{-11.25\times[-12.55-(-4.15)]\times11.25}{4.65^2}\times\frac{(10^{-18})^3}{(1.602\times10^{-12})^2}esu=114.95\times10^{-30}esu$$

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