Supporting Information

Stimulating Intra- and Intermolecular Charge Transfer and Nonlinear Optical Response for Biphenalenyl Biradicaloid Dimer under the External Electric Field

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Figure S1. The first hyperpolarizabilities ($\beta_{\text{tot}}$, au) for studied dimers at the M06-2X, the BHandHLYP and the CAM-B3LYP levels without and with the external electric field ($F_x$ and $F_z$).

Figure S1 results show that the $\beta_{\text{tot}}$ values by using the CAM-B3LYP and the BHandHLYP methods are close to that obtained by the M06-2X method under the external electric field ($F_x = 1 \times 10^{-4}$ au and $F_z = 1 \times 10^{-4}$ au).
Figure S2. The component of dipole moment ($\mu_x$ and $\mu_z$, Debye) in the ground state of IDPL dimer under the horizontal $F_x$ ($F_x = 1 \times 10^4$ au).

From Figure S2, the $\mu_x$ are sharply increased with increasing of the longitudinal $F_x$. Meanwhile, the $\mu_z$ are slightly increased with increasing of the horizontal $F_x$. 
Figure S3. The HOMO/LUMO energy levels ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, eV) (a), and HOMO-LUMO energy gap ($E_{\text{gap}}$, eV) diagrams of IDPL dimers under the horizontal $F_x$ ($F_x = 1 \times 10^{-4}$ au) (b).

Under the $F_x$, the variations of the highest occupied molecular orbital (HOMO) / the lowest unoccupied molecular orbital (LUMO) energy levels ($E_{\text{HOMO}}, E_{\text{LUMO}}$), and the HOMO-LUMO energy gap ($E_{\text{gap}}$, eV) for IDPL dimer are shown in Figure S3. When applied $F_x$ ranging from 0 to $40 \times 10^{-4}$ au, $E_{\text{LUMO}}, E_{\text{HOMO}}$ have not changed obviously. However, $E_{\text{HOMO}}$ are gradually decreased and $E_{\text{LUMO}}$ are gradually increased with the $F_x$ increasing from $40 \times 10^{-4}$ to $70 \times 10^{-4}$ au, which leads to the gradually increase of $E_{\text{gap}}$ values from 1.70 to 2.19 eV.
Figure S4. Evolutions of schematic diagrams of geometric structure (a), and curved angle of each layer of IDPL under the vertical $F_z$ (b) ($F_z = 1 \times 10^{-4}$ au).

We find that both-end nonsuperimposed PLYs of IDPL dimer present slightly curving in the opposite direction when the $F_z$ increasing from 0 to $70 \times 10^{-4}$ au in Figure S4(a). Obviously, continuing to increase the $F_z$ ranging from $70 \times 10^{-4}$ to $110 \times 10^{-4}$ au, both-end nonsuperimposed PLYs of IDPL dimer changes markedly, that is, presenting obviously upward curving in the same direction. Further, the evolutions of curved angle for each IDPL by increasing the $F_z$ are showed in Figure S4(b). At the $F_z$ increasing from 0 to $70 \times 10^{-4}$ au, the angle of end nonsuperimposed PLY with respect to middle superimposed PLY is above 5.0°. At the $F_z$ increasing from 70 to $110 \times 10^{-4}$ au, the angle of end nonsuperimposed PLY with respect to middle superimposed PLY is above 28.6°.
Figure S5. Evolutions of the interlayer distances (D, Å) of IDPL dimer under the vertical $F_z (F_z = 1 \times 10^{-4}$ au).

We mainly focus on the interlayer distance (D, Å) variation (the interlayer distance is the average distance of the six pairs of $\alpha$-carbon atoms between two layers) of IDPL dimer under the $F_z$, and corresponding results are listed in Figure S5. With increasing of the $F_z$, the interlayer distance is slightly shortened by 0.020 Å from 3.153 Å ($F_z = 0$) to 3.140 Å ($F_z = 70 \times 10^{-4}$ au). This indicates that bonding interaction for intermolecular interaction may be slightly stronger compared to that without an external electric field.
Figure S6. The component of dipole moment ($\mu_x$ and $\mu_z$, Debye) in the ground state of IDPL dimer under the vertical $F_z$ ($F_z = 1 \times 10^{-4}$ au).

From Figure S6, under the influence external electric field, the $\mu_x$ are slightly increased with increasing of the $F_z$. Meanwhile, the $\mu_z$ are slightly increased with increasing of the $F_z$. The results show that $\mu_x$ and $\mu_z$ values are very close, but directions are opposite to each other.
To gain insight into interaction between the two layers, the interaction energy ($E_{\text{int}}$ kcal mol$^{-1}$) with counterpoise (CP) is calculated under the $F_z$, as presented in Figure S7. In the absence of the external electric field, the bonding interaction between two layers results in a relative stabilization of IDPL dimer by about 18.36 kcal/mol. When the $F_z$ increases from 0 to $70 \times 10^{-4}$ au, the $E_{\text{int}}$ values between two layers of IDPL dimer are generally enhanced, which may be explained by the increase of attractive electrostatic interaction because the intermolecular CT is increased, and increase of bonding interaction because the interlayer distance is shortened. Therefore, when the external electric field is applied along the positive direction of z-axis, the interaction between two layers in IDPL dimer is mainly governed by the bonding interaction and attractive electrostatic interaction.
Table S1. The total energies ($E_{\text{M06-2X}}$ and $E_{\text{UM06-2X}}$, au) of IDPL dimer at the M06-2X and UM06-2X level with 6-31G* basis set without/under the horizontal $F_x$ ($F_x = 1 \times 10^{-4}$ au).

<table>
<thead>
<tr>
<th>$F_x \times 10^{-4}$</th>
<th>$E_{\text{M06-2X}}$</th>
<th>$E_{\text{UM06-2X}}$</th>
<th>$D_{\text{M06-2X}}$ (Å)</th>
<th>$D_{\text{UM06-2X}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>-3381.070</td>
<td>3.156</td>
<td>3.103</td>
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<tr>
<td>20</td>
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<td>-3381.076</td>
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<td>3.103</td>
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<td>-3381.094</td>
<td>-3381.094</td>
<td>3.091</td>
<td>3.091</td>
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Geometric structures of IDPL dimer without/under the horizontal $F_x$ were optimized using the broken-symmetry spin-unrestricted UM06-2X/6-31G* method. The results show that the total energy value with the UM06-2X method is slightly lower than that of the spin-restricted M06-2X method when applying small external electric field. With increasing of the $F_x$, the total energy values by using the M06-2X and the UM06-2X methods are equal. Therefore, the results obtained by using the M06-2X method are also reliable.
Table S2. The diradical characters ($\gamma$) are investigated by the (U)$\omega$B97XD/6-31G* method under the horizontal $F_x$ ($F_x = 1 \times 10^{-4}$ au).

<table>
<thead>
<tr>
<th></th>
<th>$F \times 10^{-4}$</th>
<th>$F_x = 0$</th>
<th>$F_x = 10$</th>
<th>$F_x = 20$</th>
<th>$F_x = 30$</th>
<th>...</th>
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</thead>
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<tr>
<td>monomer</td>
<td>$\gamma_0$</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>dimer</td>
<td>$\gamma_0$</td>
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<td>0.623</td>
<td>0.612</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>$\gamma_1$</td>
<td>0.120</td>
<td>0.115</td>
<td>0.102</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

The diradical characters as a function of external field amplitude have been calculated by broken symmetry (BS) spin-unrestricted scheme. In the absence of the external electric field, the $\gamma_0$ value (0.383) of the monomer has the intermediate character. The IDPL dimer has diradical character ($\gamma_0 = 0.625$) and small tetraradical character ($\gamma_1 = 0.120$). With increasing of the $F_x$, the IDPL dimer have very small diradical and tetraradical characters ($\gamma_0 = 0$ and $\gamma_1 = 0$).

References