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 (β_{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 β_{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 (μ_x and μ_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 μ_x are sharply increased with increasing of the longitudinal F_x . Meanwhile, the μ_z are slightly increased with increasing of the horizontal F_x .



Figure S3. The HOMO/LUMO energy levels (E_{HOMO} and E_{LUMO} , eV) (a), and HOMO-LUMO energy gap (E_{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_{HOMO} , E_{LUMO}), and the HOMO-LUMO energy gap (E_{gap} , eV) for IDPL dimer are shown in Figure S3. When applied F_x ranging from 0 to 40 × 10⁻⁴ au, E_{LUMO} , E_{HOMO} have not changed obviously. However, E_{HOMO} are gradually decreased and E_{LUMO} are gradually increased with the F_x increasing from 40 × 10⁻⁴ to 70 × 10⁻⁴ au, which leads to the gradually increases of E_{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 × 10⁻⁴ au in Figure S4(a). Obviously, continuing to increase the F_z ranging from 70 × 10⁻⁴ to 110 × 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 × 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 × 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 α -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 (μ_x and μ_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 μ_z are slightly increased with increasing of the F_z . Meanwhile, the μ_x are slightly increased with increasing of the F_z . The results show that μ_x and μ_z values are very close, but directions are opposite to each other.



Figure S7. Evolutions of the interaction energies (E_{int} , kcal mol⁻¹) of IDPL dimer under the vertical F_z ($F_z = 1 \times 10^{-4}$ au).

To gain insight into interaction between the two layers, the interaction energy (E_{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 × 10⁻⁴ au, the E_{int} values between two layes 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.

F×10-4	$E_{ m M06-2X}$	$E_{ m UM06-2X}$	D _{M06-2X} (Å)	D _{UM06-2X} (Å)
$F_{\rm x} = 0$	-3381.055	-3381.070	3.156	3.103
$F_{\rm x} = 20$	-3381.064	-3381.076	3.132	3.103
$F_{\rm x} = 40$	-3381.094	-3381.094	3.091	3.091

Table S1. The total energies (E_{M06-2X} and $E_{UM06-2X}$, 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).

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 (y) are investigated by the (U) ω B97XD/6-31G* method under the horizontal F_x ($F_x = 1 \times 10^{-4}$ au).

	F×10-4	$F_{\rm x} = 0$	$F_{\rm x} = 10$	$F_{\rm x} = 20$	$F_{\rm x} = 30$	
monomer	\mathcal{Y}_0	0.383				
dimer	\mathcal{Y}_0	0.625	0.623	0.612	0	0
	\mathcal{Y}_1	0.120	0.115	0.102	0	0

The diradical characters as a function of external field amplitude have been calculated by broken symmetry (BS) spin-unrestricted scheme.³ In the absence of the external electric field, the y_0 value (0.383) of the monomer has the intermediate character. The IDPL dimer has diradical character ($y_0 = 0.625$) and small tetraradical character ($y_1 = 0.120$). With increasing of the F_x , the IDPL dimer have very small diradical and tetraradical characters ($y_0 = 0$ and $y_1 = 0$).

References

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