Supporting Information

Tuning inter-molecular charge transfer, second-order nonlinear optical and absorption spectra properties of π-dimer under the external electric field

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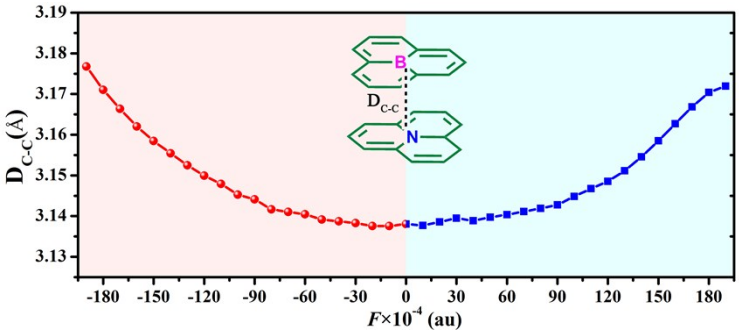

Figure S1. Evolutions of the distances between the boron and nitrogen atoms (D, [Å]) of PLY_2-BN under the F ($F = 1 \times 10^{-4}$ au).

Figure S1 presents the evolution of the distance between the boron and nitrogen atoms with the different strength of external electric fields. Obviously, the change trend of distances with F along direction of negative z-axis is consistent with the distances with F along direction of positive z-axis, and they are gradually increased.

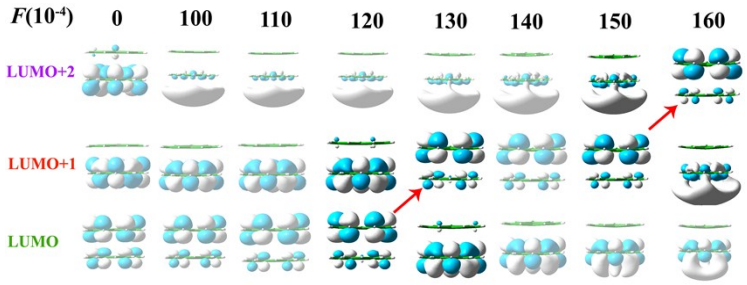

Figure S2. Evolutions of frontier molecular orbital (FMO) of BN-PLY$_2$ under the F along direction of positive z-axis (F = 1 × 10^{-4} au).

Figure S2 shows that the evolutions of the lowest unoccupied molecular orbital (LUMO) under the F. When the F_{+z} ranging from 120 to 130 × 10^{-4} au, the LUMO and the LUMO +1 takes place orbital interchange. When F continues to increase from 150 × 10^{-4} to 160 × 10^{-4} au, LUMO+1 and LUMO +2 exhibit orbital interchange in π-dimer, corresponding evolutions of FMOs of BN-PLY$_2$ under the F are presented in Figure S2.

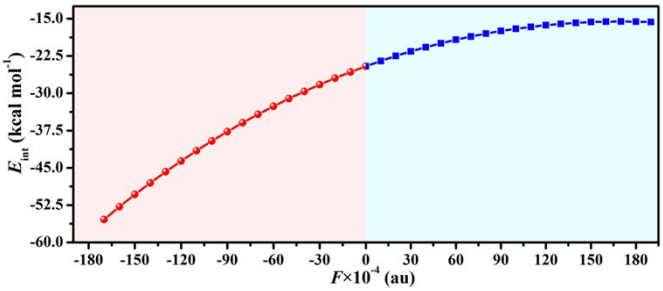

Figure S3. Evolutions of the interaction energy (E_{int}, kcal mol^{-1}) of BN-PLY$_2$ under the F ($F = 1 \times 10^{-4}$ au) by using the M06-2X with D3 method.

The dispersion-corrected is very important for evaluating interactions of π-dimer systems. Therefore, we use M06-2X-D3 method to calculate interaction energy (E_{int}, kcal mol^{-1}) of BN-PLY$_2$ in Figure S3. It can be clearly seen that tend of the E_{int} values calculated by using the M06-2X-D3 method are consistent with that of the M06-2X method, and the E_{int} value with the M06-2X-D3 method increase of above 1.5 kcal mol^{-1} compared to M06-2X method.

Table S1. The first hyperpolarizabilities (β_{tot}, au) and the components of first hyperpolarizabilities for π-dimers under the F ($F = 1 \times 10^{-4}$ au) by using the M06-2X method with different basis sets (6–31+G**, 6–31+G*, 6–31++G** and 6–311+G**).

Basis set		-190	-150	-100	-50	0	50	100	150	190
6–31+G**	β_x	12.85	7.05	1.22	-2.53	-7.22	-6.70	-6.33	-1.74	0.31
	β_y	1.80	-1.55	-5.96	-8.32	3.07	-10.70	-8.78	7.17	26.94
	β_z	4.07×10^3	3.24×10^3	2.85×10^3	2.85×10^3	3.02×10^3	3.00×10^3	2.05×10^3	-9.14×10^2	-6.67×10^3
	β_{tot}	4.07×10^3	3.24×10^3	2.85×10^3	2.85×10^3	3.02×10^3	3.00×10^3	2.05×10^3	9.14×10^2	6.67×10^3
6–31+G*	β_x	12.52	6.86	1.10	-2.55	-5.98	-6.57	-6.21	-1.79	0.16
	β_y	1.66	-1.43	-5.50	-7.46	3.01	-9.29	-7.55	7.69	26.71
	β_z	4.10×10^3	3.26×10^3	2.86×10^3	2.86×10^3	3.04×10^3	3.01×10^3	2.05×10^3	-9.13×10^2	-6.67×10^3
	β_{tot}	4.10×10^3	3.26×10^3	2.86×10^3	2.86×10^3	3.04×10^3	3.01×10^3	2.05×10^3	9.13×10^2	6.67×10^3
6–31++G**	β_x	12.75	6.65	1.08	-2.54	-7.22	-6.74	-6.46	-1.42	1.79
	β_y	3.40	-1.73	-6.25	-8.36	3.03	-10.88	-9.21	7.78	31.86
	β_z	4.29×10^3	3.34×10^3	2.87×10^3	2.83×10^3	2.98×10^3	2.93×10^3	1.95×10^3	-1.07×10^3	-6.90×10^3
	β_{tot}	4.29×10^3	3.34×10^3	2.87×10^3	2.83×10^3	2.98×10^3	2.93×10^3	1.95×10^3	1.07×10^3	6.90×10^3
6–311+G**	β_x	10.95	6.42	0.90	-3.02	-6.44	-7.35	-6.84	-1.81	0.52
	β_y	-2.29	-4.95	-7.52	-8.33	3.60	-10.29	-11.27	-3.70	3.33
	β_z	3.59×10^3	2.96×10^3	2.73×10^3	2.80×10^3	3.01×10^3	2.99×10^3	2.10×10^3	-7.02×10^2	-6.56×10^3
	β_{tot}	3.59×10^3	2.96×10^3	2.73×10^3	2.80×10^3	3.01×10^3	2.99×10^3	2.10×10^3	7.02×10^2	6.56×10^3

We used the M06-2X results to further evaluate the effect of the different basis sets on the second-order NLO properties, so four basis sets (6-31+G*, 6-31+G**, 6-31++G**, and 6-311+G**) were chosen to calculate the β_{tot} value under the F. Obviously, the different basis sets obtain the same trend in the β_{tot} value, and the β_{tot} values are very close. The above results confirm the reliability and accuracy of 6-31+G** basis set.

Table S2. The first hyperpolarizabilities (β_{tot}, au) and the components of first hyperpolarizabilities for π-dimers under the F ($F = 1 \times 10^{-4}$ au) at the M06-2X/6–31+G** level.

	β_x	β_y	β_z	β_{tot}
-190	12.85	1.80	4.07×10^3	4.07×10^3
-150	7.05	-1.55	3.24×10^3	3.24×10^3
-100	1.22	-5.96	2.85×10^3	2.85×10^3
-50	-2.53	-8.32	2.85×10^3	2.85×10^3
0	-7.22	3.07	3.02×10^3	3.02×10^3
50	-6.70	-10.70	3.00×10^3	3.00×10^3
100	-6.33	-8.78	2.05×10^3	2.05×10^3
150	-1.74	7.17	-9.14×10^2	9.14×10^2
190	0.31	26.94	-6.67×10^3	6.67×10^3

Table S2 results show that the β_z values are very close to the β_{tot} values under the F, indicating that the greatest contribution to the β_{tot} is the β_z value for π-dimer.