Supporting Information

Describing Curved-Planar π-π Interactions: Modeled by Corannulene, Pyrene and Coronene

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SI 1: The visualization details:

The wave functions were generated by Gaussian09 at B97D/TZVP level.

Multiwfn2.6 deals with reduced density gradient (RDG) in real space as equal 1:

$$RDG(r) = \frac{1}{2*(3*\pi^2)^{\frac{1}{3}}} * \frac{|\nabla\rho(r)|}{\rho(r)^{\frac{4}{3}}} \quad (1)$$

Where ρ(r) is electron density and can be defined as equal 2， $\nabla\rho(r)$ is the electron density gradient.

$$\rho(r) = \sum_i \eta_i |\varphi_i(r)|^2 = \sum_i \eta_i \left| \sum_l C_{l,i}\chi_l(r) \right|^2 \quad (2)$$

Where φ is orbital wave function generated by B97D/TZVP mentioned above, η_i is occupation number of orbital *i*, χ is basis function. *C* is coefficient matrix, the element of i^{th} row j^{th} column corresponds to the expansion coefficient of orbital *j* respect to basis function *i*. The other details of Multiwfn2.6 are in the web: http://multiwfn.codeplex.com/

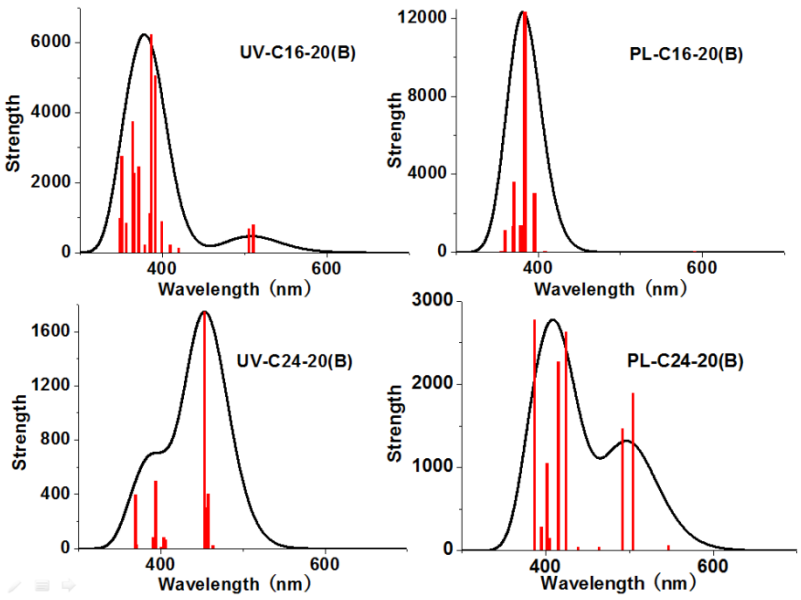

Figure S2. Absorption (left) and photoluminescence emission (right) spectra of C16-20(B) (top) and C24-20(B) (down) complexes.

SI 3: The details of transfer integral.

The HOMO (LUMO) of C16, C20, C24 are 53 (54), 65 (66), 78 (79) respectively. The MO1 (MO2) is the orbital number of the former (latter) monomer in dimer/complex, e1 (e2) is the energy of the orbital (eV). t is the transfer integral (meV). If there have degenerate/near-degenerate orbitals, the transfer integral (effective coupling) was calculated by the equal:

$$t = \sqrt{t_1^2 + t_2^2 + t_3^2 ... t_i^2} \quad (3)$$

Where t_i is the transfer integral of each relative orbital.

C16-16:

MO1	MO2	e1	e2	t
53	53	-4.859	-4.859	114.599
54	54	-2.224	-2.224	-123.966

C16-20(B):

MO1	MO2	e1	e2	t
53	64	-4.770	-5.382	-13.042
53	65	-4.770	-5.379	-27.256

Effective coupling = 30.216

MO1	MO2	e1	e2	t
54	66	-2.127	-2.334	25.801
54	67	-2.123	-2.321	133.212

Effective coupling = 135.688

C16-20(M):

MO1	MO2	e1	e2	t
53	64	-4.988	-5.475	0.056
53	65	-4.988	-5.442	-10.930

Effective coupling = 10.930

MO1	MO2	e1	e2	t
54	66	-2.348	-2.408	49.268
54	67	-2.348	-2.412	-0.587

Effective coupling = 49.271

C16-24:

MO1	MO2	e1	e2	t
53	77	-4.784	-5.028	132.324
53	78	-4.784	-5.029	129.726

Effective coupling = 185.306

MO1	MO2	e1	e2	t
54	79	-2.148	-2.153	-15.269
54	80	-2.143	-2.147	158.257

Effective coupling = 158.992

C24-24:

MO1	MO2	e1	e2	t
77	77	-4.993	-4.993	-50.139
77	78	-4.993	-4.995	-16.218
78	77	-4.995	-4.993	0.677
78	78	-4.989	-4.989	179.154

Effective coupling = 186.745

MO1	MO2	e1	e2	t
79	79	-2.116	-2.120	80.060

79	80	-2.117	-2.113	52.085
80	79	-2.117	-2.121	51.510
80	80	-2.117	-2.112	-80.664

Effective coupling = 135.212

C24-20(B):

MO1	MO2	e1	e2	t
77	64	-4.944	-5.344	-31.572
77	65	-4.945	-5.341	1.395
78	64	-4.944	-5.344	2.751
78	65	-4.944	-5.341	-6.124

Effective coupling = 32.308

MO1	MO2	e1	e2	t
79	66	-2.066	-2.298	13.553
79	67	-2.064	-2.292	79.849
80	66	-2.063	-2.298	3.874
80	67	-2.063	-2.294	-7.743

Effective coupling = 81.452

C24-20(M):

MO1	MO2	e1	e2	t
64	77	-5.352	-5.174	-34.373
64	78	-5.351	-5.175	64.130
65	77	-5.346	-5.174	-2.269
65	78	-5.346	-5.176	10.760

Effective coupling = 73.587

MO1	MO2	e1	e2	t
66	79	-2.294	-2.297	38.915
66	80	-2.294	-2.297	6.497
67	79	-2.288	-2.297	7.018
67	80	-2.284	-2.294	132.794

Effective coupling = 138.709

Table S4. The Raman data of the oxidation-state of the planar (C16) and curved molecules (C20), and in P-P dimer (C16-16), C_B-P [C16-20(B)] and C_M-P [C16-20(M)] complexes.

	C16	C20	C16-16	C16-20(B)	C16-20(M)
C16 wavelength[a]	1417.7	-	1405.3[b]	1419.3	1423.9
C16 intensity	222.41	-	286.31	97.24	108.79
C16 Raman shift[a,b]	-	-	-12.4	1.6	6.2
C20 wavelength	-	1435.5	-	1439.9	1435.0
C20 intensity	-	361.44	-	227.91	143.59
C20 Raman shift	-	-	-	4.4	-0.5

[a] Unit is cm^{-1}. [b] Raman peak position of dimer/complex originating from the isolated monomer. [c] Raman shift between the isolated monomer and corresponding monomer in dimer/complex. Table S 5 is the same.

Table S5. The Raman data of the oxidation-state of the planar (C24) and curved molecules (C20), and in P-P dimer (C24-24), C_B-P [C24-20(B)] and C_M-P [C24-20(M)] complexes.

	C24	C20	C24-24	C24-20(B)	C24-20(M)
C24 wavelength	1356.7	-	1322.1	1362.1	1363.1
C24 intensity	874.86	-	754.26	466.23	483.16
C24 raman shift		-	-34.6	5.4	6.4
C20 wavelength	-	1435.5	-	1436.6	1435.8
C20 intensity	-	361.45	-	168.95	184.53
C20 Raman shift		-	-	1.1	0.3