Electronic Supplementary Material (ESI) for

Star-shaped Carbazole-based BODIPY Derivatives with Improved Hole Transportation and Near-infrared Absorption for Small-Molecule Organic Solar Cells with High Open-Circuit Voltages

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General Method

Relative quantum efficiencies of fluorescence of compounds are obtained by comparing the areas under the corrected emission spectrum of the test sample in diluted solvents with that of Rhodamine B (Φ_F = 0.69) in methanol and a reported aza-BODIPY derivative in toluene which has a quantum efficiency of 0.42 according to the literature.[1] Non-degassed, spectroscopic grade toluene and a 10 mm quartz cuvette are used. Dilute solutions (0.01 < A < 0.05) are used to minimize reabsorption effects. Quantum yields are determined using the equation (1):

$$\Phi_F^{(sample)} = \Phi^{(standard)} \times (Abs^{(standard)} \times F^{(sample)}) / (Abs^{(sample)} \times F^{(standard)}) \quad \text{equation (1)}$$

Where $\Phi^{(standard)}$ is the reported quantum yield of the standard, Abs is the absorbance at the excitation wavelength, F is the integrated emission spectra.
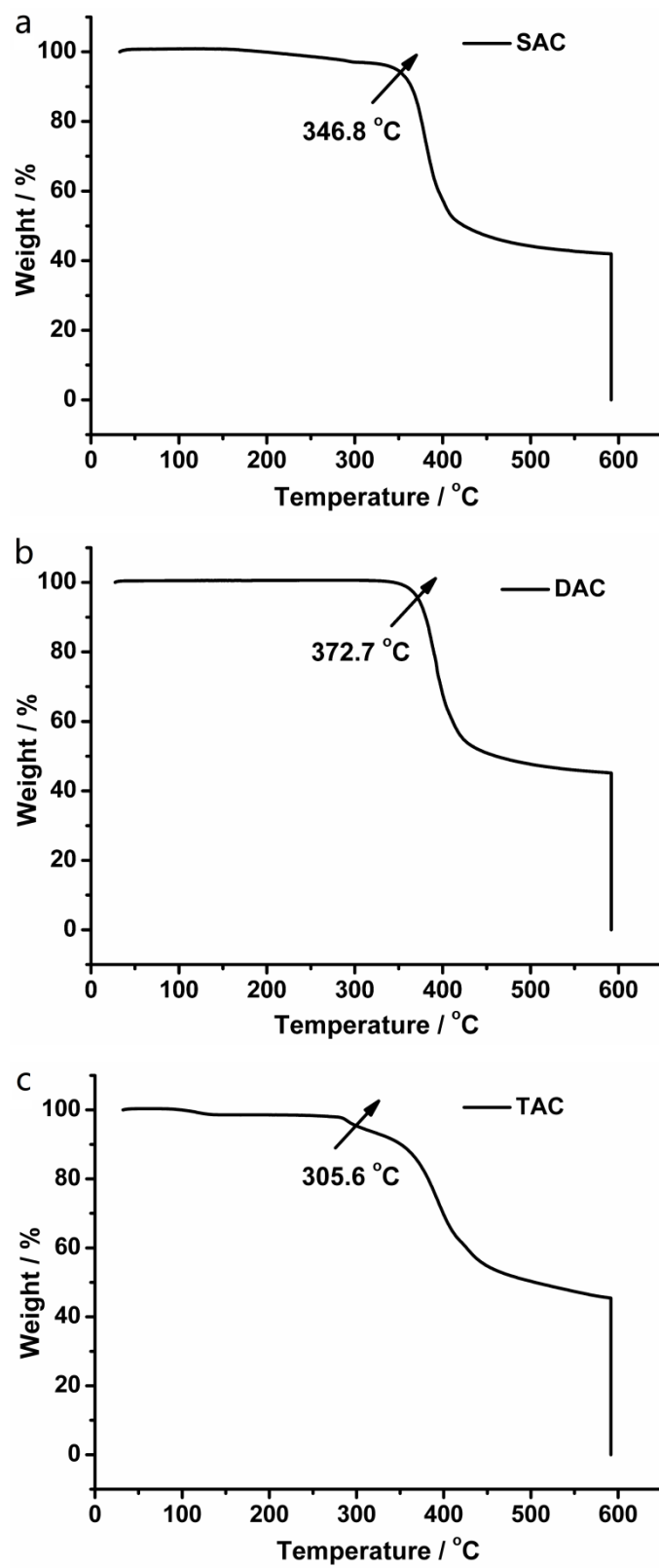
Fig. S1 TGA thermograms of (a) **SAC**, (b) **DAC** and (c) **TAC** measured under nitrogen flow (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹.
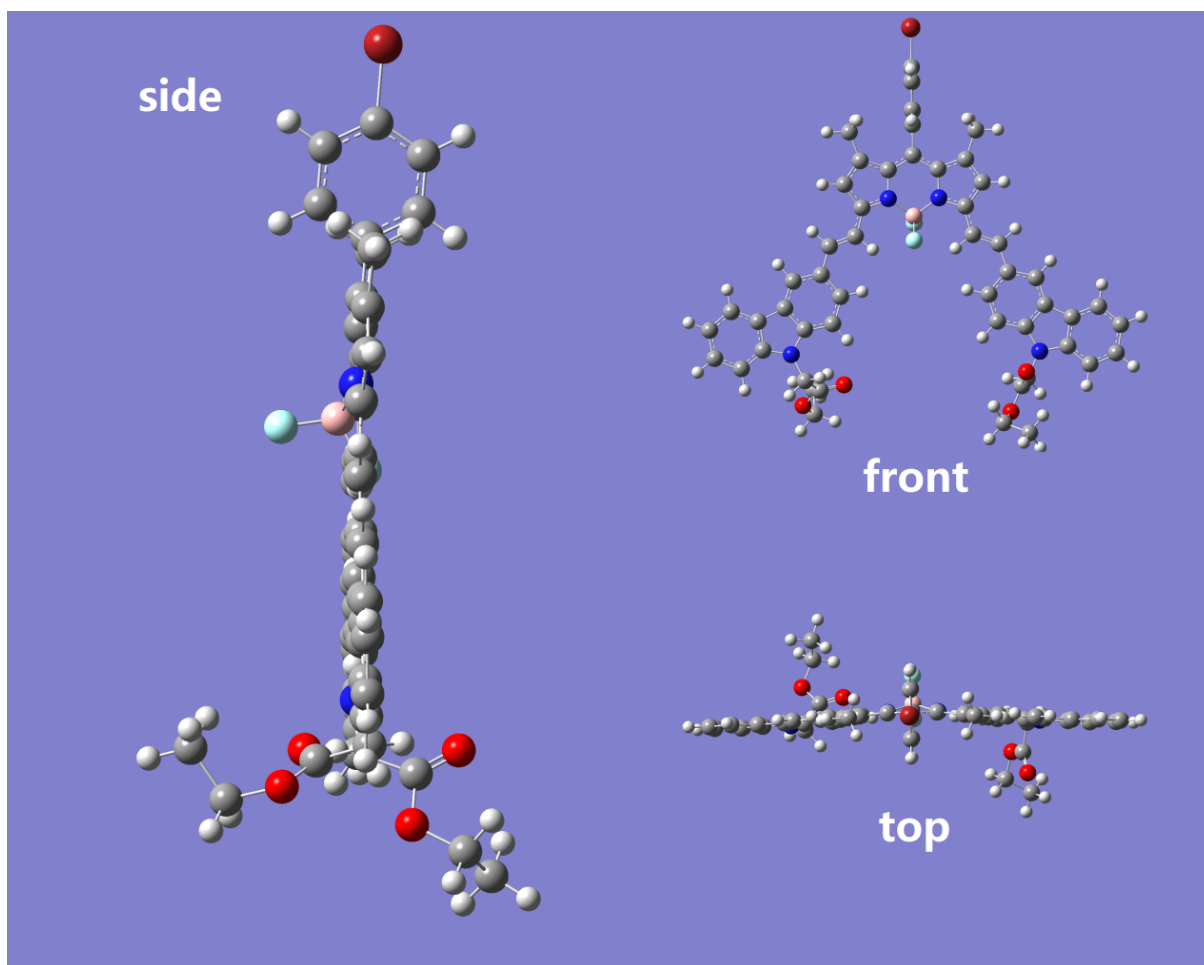
Fig. S2 Structure of **DAC** optimized by DFT calculation.
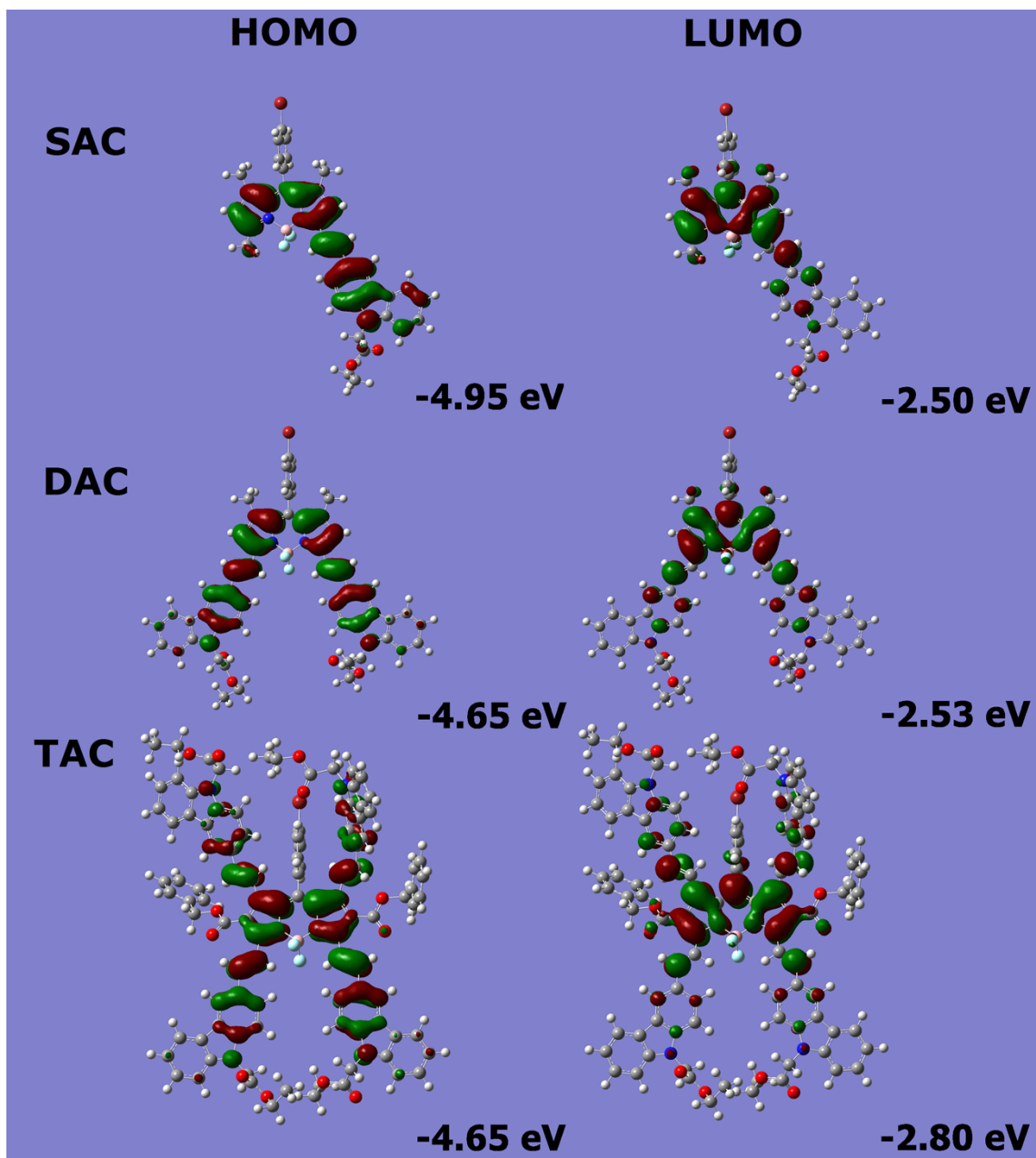
Fig. S3 Theoretically calculated HOMO and LUMO electron distribution of **SAC**, **DAC** and **TAC**.

Table S1 Photophysical properties of **SAC**, **DAC**, **TAC** in toluene.

Dye	λ_{abs}/nm	λ_{em}/nm	ε/(M^{-1} cm^{-1})	Φ_f
SAC	590	609	102000	0.62[a]
DAC	674	692	121000	0.98[b]
TAC	728	755	135000	0.42[b]

[a] Rhodamine B is used as standard. [b] Reported 3, 5-bi (p–methoxy) phenyl-1, 7-bi (p-bromo) phenyl aza-BODIPY (Φ_f = 0.42, in tolunene) is used as standard.
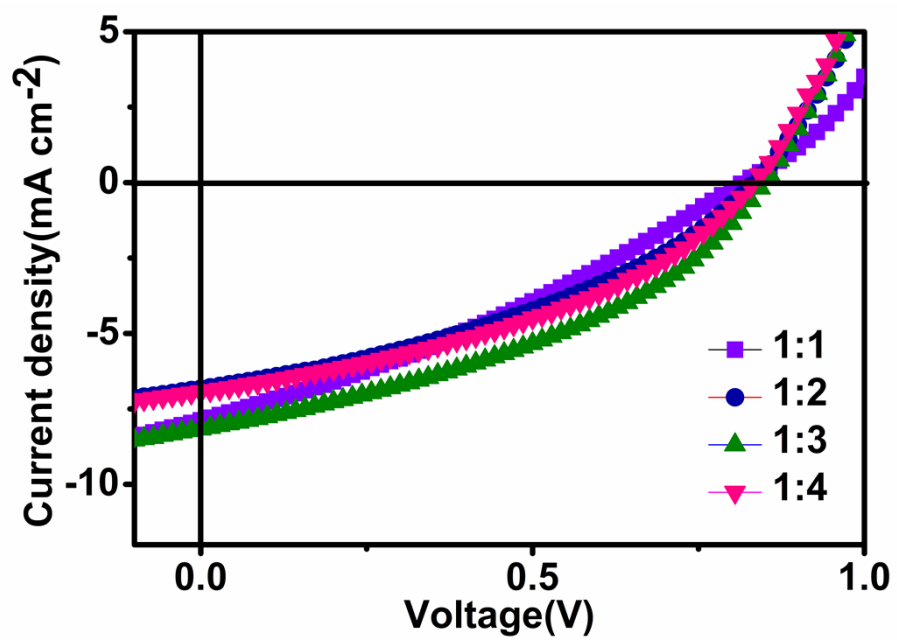
Fig. S4 Current density-voltage (*J-V*) curves of the OSCs based on **TAC** and PC$_{61}$BM with different weight ratios.
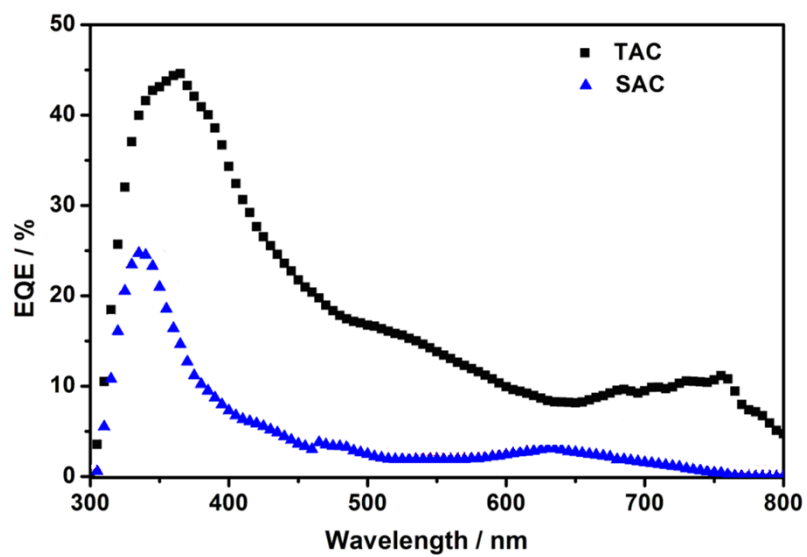
Fig. S5 The external quantum efficiencies (EQE) of **TAC (SAC)**:$PC_{61}BM$ at a weight ratio of 1:3.
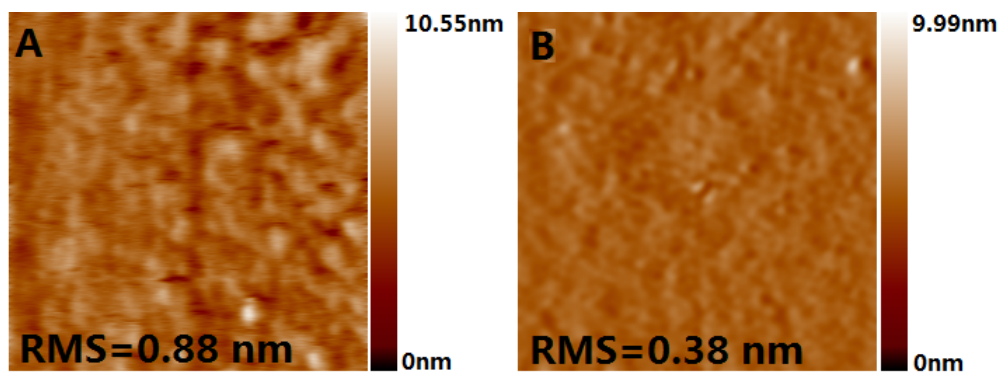
Fig. S6 AFM height images (5μm × 5μm) of the active layers based on (A) **SAC:**$PC_{61}BM$, (B) **TAC:**$PC_{61}BM$.

SAC

8.68
7.67
7.65
7.50
7.49
7.36
7.34
7.32
7.24
7.22
6.68
6.02
5.30
5.01
4.25
4.23
4.21
4.19
2.63
1.50
1.44
1.25
1.23
1.22

8   6   4   2   0

SAC

168.2
154.5
154.3
141.0
132.4
130.2
126.4
126.0
123.2
120.8
120.4
120.3
108.8
78.7
77.3
77.2
77.0
76.7
61.8
44.9
15.0
14.7
14.6
14.1
0.0

200   100   0

DAC

8.22
8.20
7.84
7.68
7.66
7.52
7.51
6.72

5.02

4.26
4.24
4.22
4.20

1.52
1.26
1.24
1.23

8   6   4   2   0

DAC

168.2

153.2

141.2
141.0
137.7
132.3
130.6
128.8
126.4
126.0
123.8
123.3
120.9
120.3
120.2
117.8
108.8
108.7

61.7

44.9

15.0
14.2

200   100   0

TAC

8.16
8.15
8.12
8.10
7.73
7.69
7.67
7.57
7.50
7.48
7.38
7.36
7.34
7.22
7.14
6.94
6.89
6.79
5.85
5.01
4.98
4.24
4.22
4.21
4.19
1.25
1.24
1.23
1.21
−0.00

10 5 0

TAC

168.4
168.1
167.5
151.9
141.7
141.2
141.1
140.9
140.7
135.9
135.3
132.9
132.8
132.3
129.0
128.9
128.7
128.6
128.6
126.5
126.4
126.2
124.6
123.9
123.7
123.5
123.3
121.8
121.2
121.1
120.5
120.2
119.9
117.9
115.8
109.0
108.8
108.7
67.7
62.0
61.9
45.1
45.1
14.4

200 150 100 50 0

S12