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 ($\Phi_F = 0.69$) 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):

$$\Phi_F^{(\text{sample})} = \Phi^{(\text{standard})} \times \frac{(\text{Abs}^{(\text{standard})} \times F^{(\text{sample})})}{(\text{Abs}^{(\text{sample})} \times F^{(\text{standard})})}$$  

Equation (1)

Where $\Phi^{(\text{standard})}$ 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.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{abs}}$/nm</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\varepsilon$/(M$^{-1}$ cm$^{-1}$)</th>
<th>$\Phi_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>590</td>
<td>609</td>
<td>102000</td>
<td>0.62$^{[a]}$</td>
</tr>
<tr>
<td>DAC</td>
<td>674</td>
<td>692</td>
<td>121000</td>
<td>0.98$^{[b]}$</td>
</tr>
<tr>
<td>TAC</td>
<td>728</td>
<td>755</td>
<td>135000</td>
<td>0.42$^{[b]}$</td>
</tr>
</tbody>
</table>

[a] Rhodamine B is used as standard. [b] Reported 3, 5-bi (p–methoxy) phenyl-1, 7-bi (p-bromo) phenyl aza-BODIPY ($\Phi_t = 0.42$, in toluene) 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.