

## The Position and Frequency of Fluorine Atoms Changes the Electron Donor/Acceptor Properties of Fluorophenoxy Silicon Phthalocyanines within Organic Photovoltaic Devices

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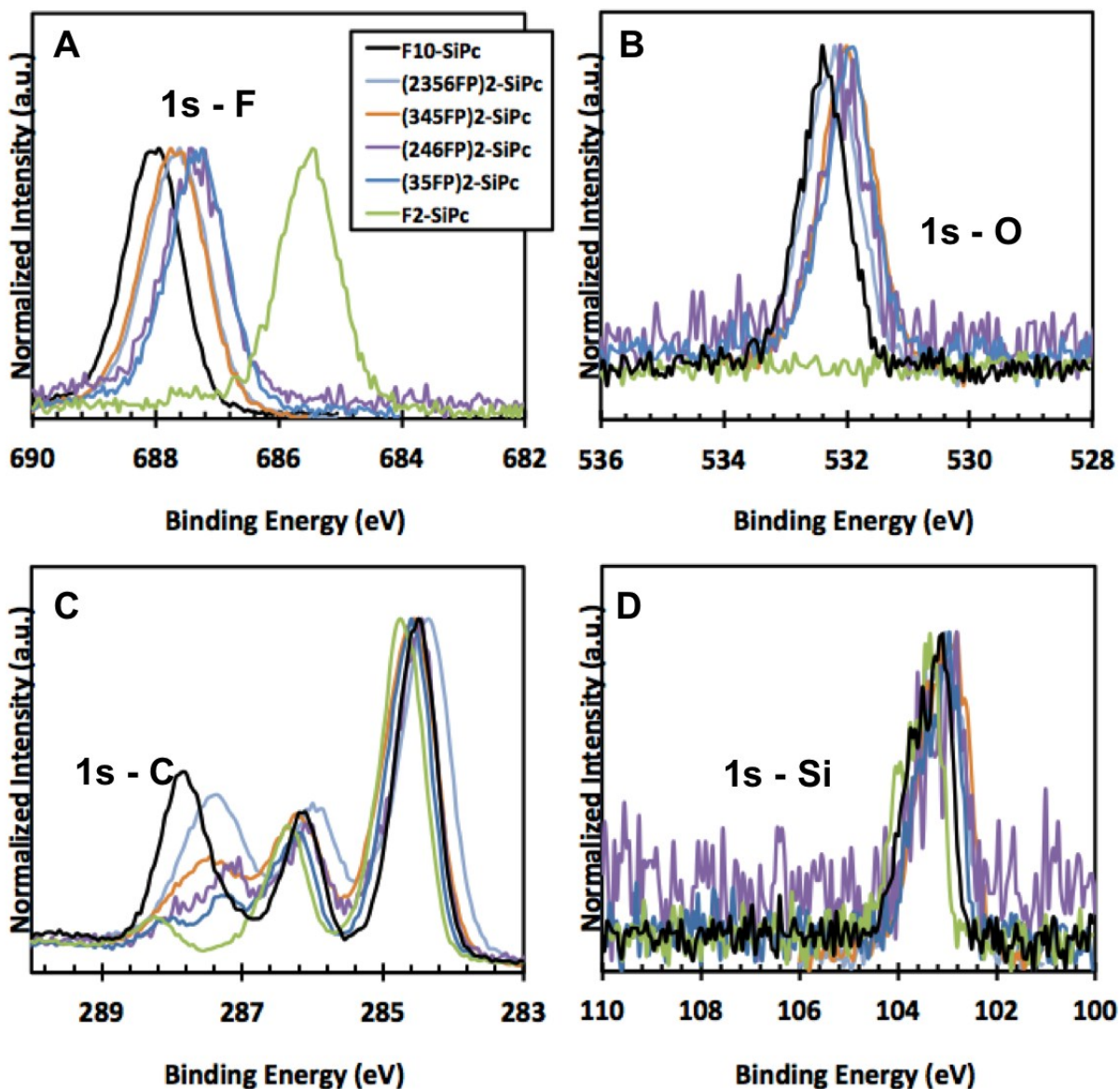
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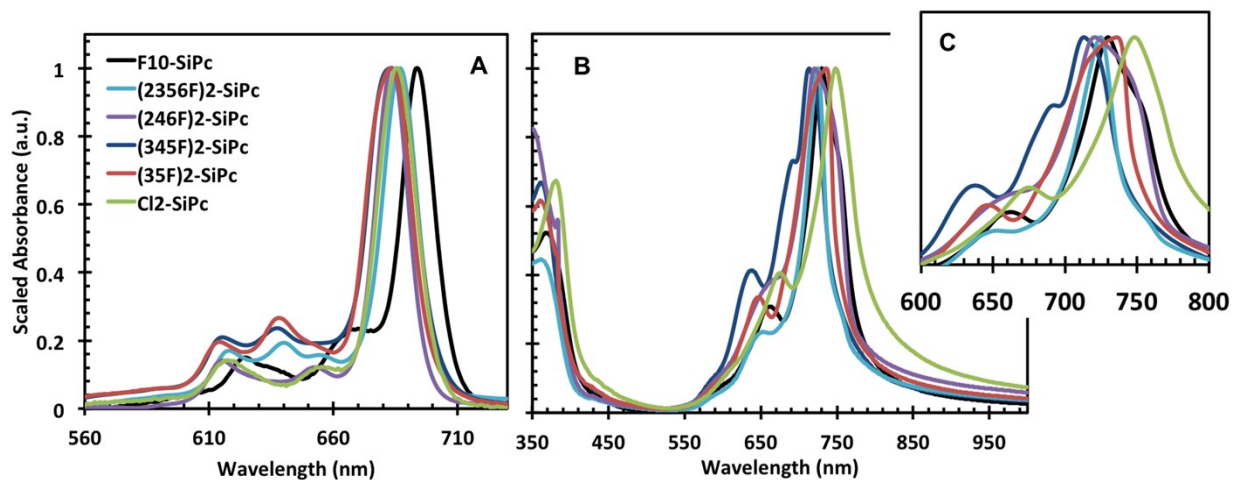
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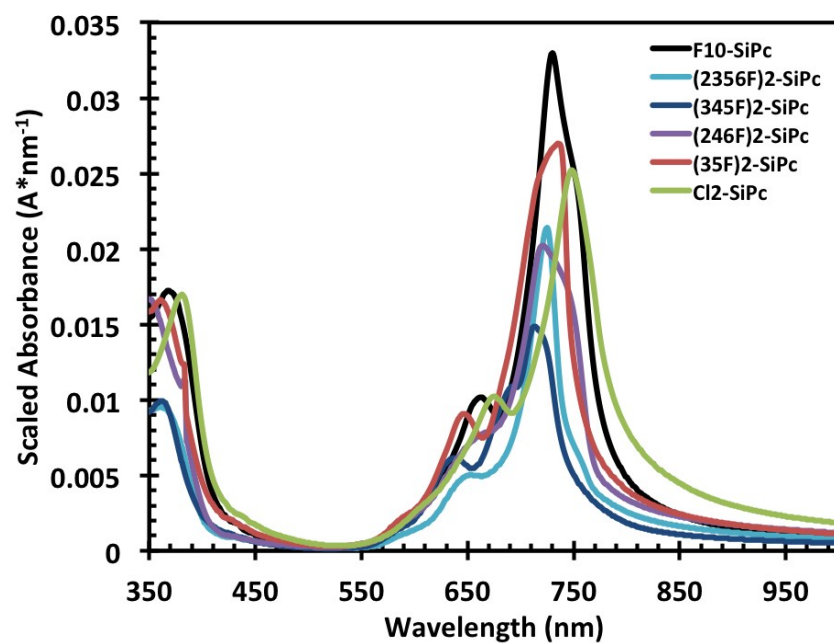
# Electronic Supporting Information.



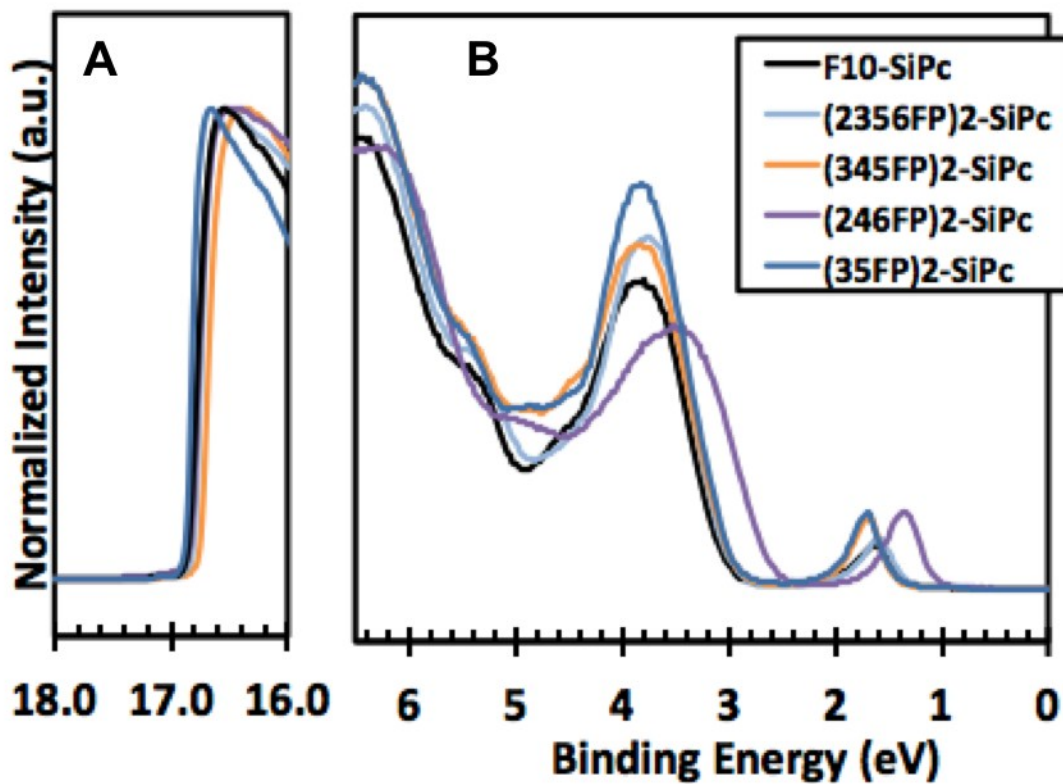
**Figure S1.** Core level x-ray photoelectron spectroscopy (XPS) for the fluorophenoxy silicon phthalocyanine where A) is a close of the peaks associated to the 1s orbital of the fluorine, B) is the peaks associated to the 1s orbital of oxygen, C) is the peaks associated to the 1s orbital of the carbon and D) is the peaks associated to the 1s orbital of the silicon. The legend in A) is the same for B), C) and D).



**Figure S2** – Normalized absorbance (a.u.) A) in Toluene and B) from thin films obtained by thermal evaporation of Cl<sub>2</sub>-SiPc and the fluorophenoxy derived SiPc's. C) is an enlargement of the peaks in B). The legend in A) is the same for B) and C).



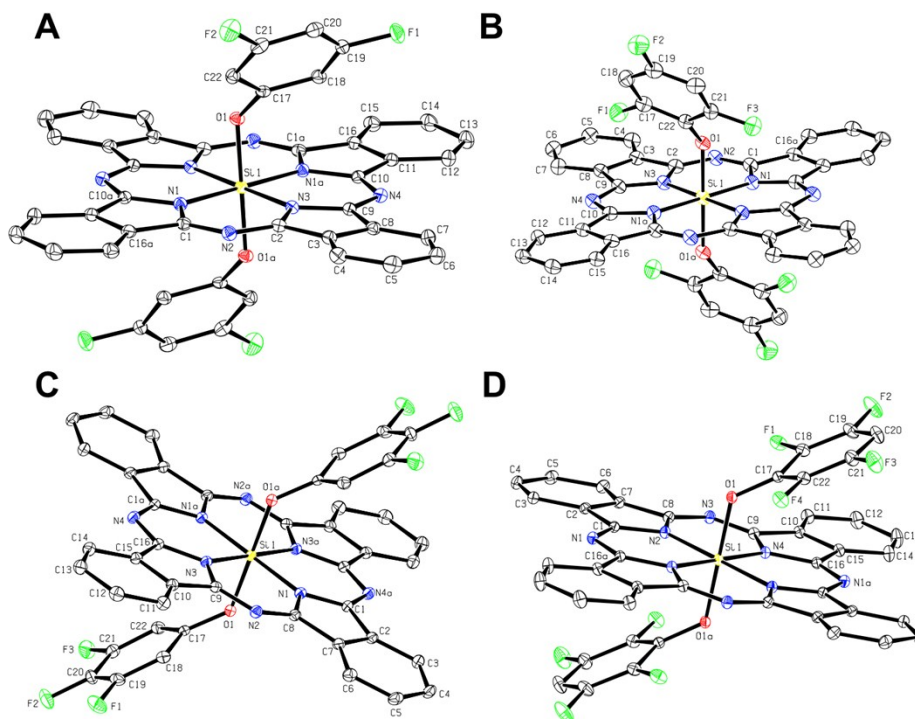
**Figure S3** – Thickness scaled absorbance ( $A \cdot \text{nm}^{-1}$ ) of thin films obtained by thermal evaporation of  $\text{Cl}_2$ -SiPc and the fluorophenoxy derived SiPc's. The film thickness was determined by stylus profilometry.



**Figure S4** Ultraviolet photoelectron spectroscopy (UPS) for the fluorophenoxy silicon phthalocyanine where A) is a close of the high binding energy peak used to determine the work function and B) are the low binding energy peaks used to determine the HOMO offset. The legend in B) is the same for A).

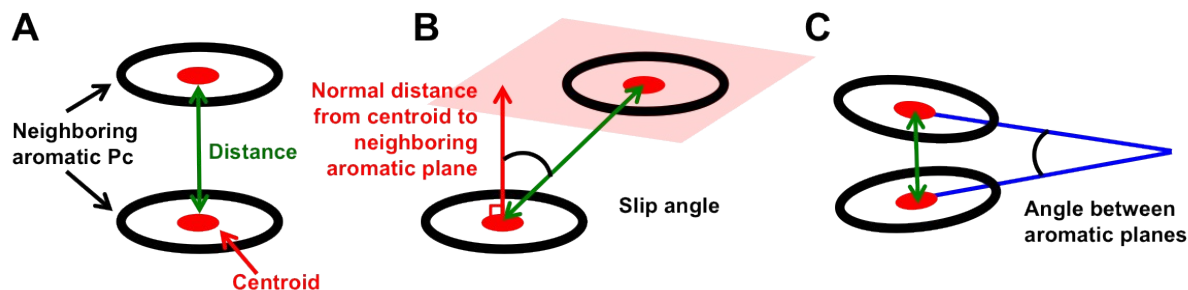
### Single Crystals of (XF)<sub>2</sub>-SiPcs.

As mentioned in the manuscript, single crystals of all (XF)<sub>2</sub>-SiPcs derivatives were grown by slow diffusion of heptane into THF. These single crystals were subsequently diffracted using X-ray crystallography and the resulting thermal ellipsoid plots can be found in **Figure S5**. The solid state packing and arrangement of these molecules were analyzed and compared against Cl<sub>2</sub>-SiPc and F<sub>10</sub>-SiPc; the results of which are tabulated in **Table S1**. We focused on three major metrics for determining the level of  $\pi$ - $\pi$  interactions: the shortest distance between the centroid of the aromatic groups on neighboring SiPcs (**Figure S6A**), the slip angle between the aromatic groups and the angle between the two planes which encompass these aromatic groups. The slip angle is depicted in **Figure S6B** as the angle between the line that connects the two centroids (green line) and the line that is normal to the centroid; if the two aromatic groups were perfectly superimposed (and they were parallel to each other), then the slip angle would be equal to 0°. It should also be noted that if the aromatic groups themselves are not parallel (**Figure S6C**) then there would be two different slip angles for the pair of aromatic groups depending on which normal was used to define the angle (**Figure S6B**). Further information on the obtained crystal diffractions such as density and unit cell size can be found in the supporting information (**Table S2**). Considering these metrics, the crystal structure of Cl<sub>2</sub>-SiPc (CCDC deposit# 173621 and 148330, code: VIKVEQ and VIKVEQ01, taken from Kojima et al.<sup>51</sup> and Silver et al.<sup>52</sup>) was characterized by having two minor interactions: the first with a shortest distance between benzene rings on the SiPc of 3.977 Å with a minimum angle between the aromatic planes of 16.69° and a slip angle of 34.34°/36.11° and the second with a shortest distance between benzene rings on the phthalocyanine of 4.172 Å with a minimum angle between the aromatic planes of 1.72° and a slip angle of 34.87°/36.59° (**Table S1**).



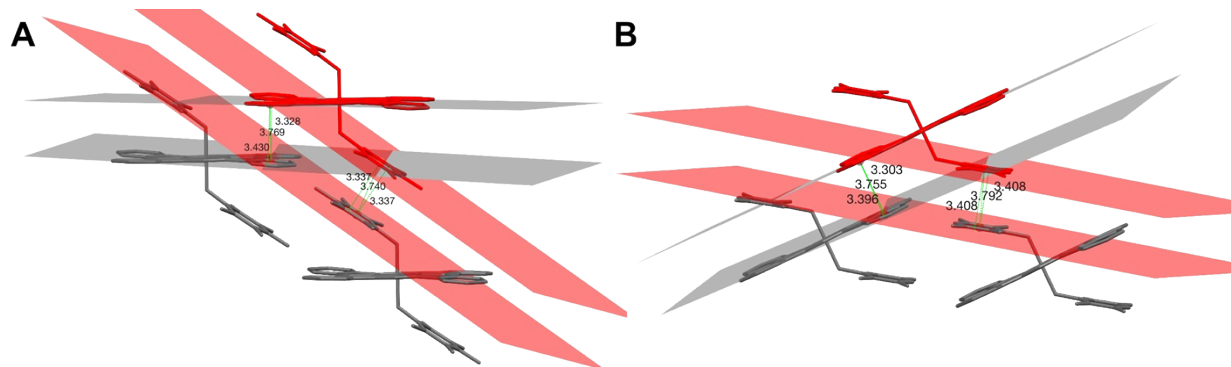
**Figure S5** – Molecular structure determined by single crystal X-ray crystallography where the size of the ellipsoids are at 50% probability for A) (35F)<sub>2</sub>-SiPc, B) (246F)<sub>2</sub>-SiPc, C) (345F)<sub>2</sub>-SiPc and D) (2356F)<sub>2</sub>-SiPc, respectively.

Generally, the solid-state arrangement was improved with for all (XF)<sub>2</sub>-SiPcs when compared against Cl<sub>2</sub>-SiPc. **Figure 5** illustrates the major packing interaction motifs for (35F)<sub>2</sub>-SiPc, (345F)<sub>2</sub>-SiPc, (246F)<sub>2</sub>-SiPc and (2356F)<sub>2</sub>-SiPc. Depending on the nature of the fluorophenoxy fragment a different solid-state arrangement was identified each having a varying degree of interactions between SiPc chromophores (**Figure 5**). For example, (2356F)<sub>2</sub>-SiPc has a parallel stacking of two of the peripheral aromatic groups of the SiPcs (**Figure 5A**) similar to that of F<sub>10</sub>-SiPc.<sup>32</sup> F<sub>10</sub>-SiPc and (2356F)<sub>2</sub>-SiPc have similar slip angles between SiPc chromophores and angles between the aromatic planes (**Figure S7, Table S1**). There is a more significant interaction (low slip angle and low distance) between the pentafluorophenoxy fragments of the F<sub>10</sub>-SiPc resulting in less significant interaction between the SiPc rings. Conversely, (2356F)<sub>2</sub>-SiPc has a less significant phenoxy fragment interaction and a more significant interaction between SiPc rings (**Figure S7, Table S1**). No interactions between phenoxy groups were observed (for (35F)<sub>2</sub>-SiPc, (345F)<sub>2</sub>-SiPc and (246F)<sub>2</sub>-SiPc crystal structures). (35F)<sub>2</sub>-SiPc and (246F)<sub>2</sub>-SiPc both have similar dual aromatic ring interaction as F<sub>10</sub>-SiPc and (2356F)<sub>2</sub>-SiPc except in both cases there were no significant interactions between the phenoxy groups. (35F)<sub>2</sub>-SiPc and (246F)<sub>2</sub>-SiPc have a parallel stacking of two of the peripheral aromatic units of the SiPc chromophore, with very similar molecular distances of 3.818 Å and 3.860 Å, respectively, suggesting similar strength in  $\pi$ - $\pi$  interactions between neighboring molecules for both (35F)<sub>2</sub>-SiPc and (246F)<sub>2</sub>-SiPc (**Figure 5, Table S1**). (35F)<sub>2</sub>-SiPc has a slip angle of 24.07°/22.75° with 1.32° between the aromatic planes while (246F)<sub>2</sub>-SiPc has a more significant slip angle of 30.08° and completely parallel (0° between planes) and interacting aromatic groups (**Figure 5, Table S1**). (345F)<sub>2</sub>-SiPc has a unique stacking of the entire aromatic isoindoline group of the SiPcs, with shortest molecular distances of 3.580 Å, indicating strong  $\pi$ - $\pi$  interactions between neighboring (345F)<sub>2</sub>-SiPcs (**Figure 5, Table S1**). In addition, the (345F)<sub>2</sub>-SiPc experience a small slip angle of 18.90° and completely parallel (0° between planes) and interacting isoindoline groups (**Figure 5, Table S1**). These results represent strong  $\pi$ - $\pi$  interactions between the SiPc chromophores that are very different from F<sub>10</sub>-SiPc, (2356F)<sub>2</sub>-SiPc, (35F)<sub>2</sub>-SiPc or (246F)<sub>2</sub>-SiPc.



**Figure S6.** Graphical representations of the criteria used to quantify the aromatic interactions between neighboring MPC molecules: (A) the distance between the aromatic groups on these neighboring MPCs, (B) the slip angle between these aromatic groups and (C) the smallest angle between the two planes which harbour these aromatic groups.

The sum of these results generally indicate that for all cases, significant increases in the  $\pi$ - $\pi$  interactions between SiPc chromophores is achieved in the solid-state arrangement when a phenoxy fragment replaces the chloride atom of Cl<sub>2</sub>-SiPc molecule. However, depending on the structure of the phenoxy fragment, the position and frequency of the fluorine atoms, the resulting (XF)<sub>2</sub>-SiPcs have significant differences in both the  $\pi$ - $\pi$  interactions of the SiPc chromophores and in their overall solid-state arrangement.



**Figure S7** – Crystal structure organizations of A)  $F_{10}$ -SiPc and B)  $(2356FP)_2$ -SiPc obtained by single crystal x-ray diffraction. The grey planes run through the aromatic Pc groups that are being studied and the red planes run through the phenoxy groups. The dotted green lines represent either the molecular  $\pi$ - $\pi$  interactions between neighboring molecules ( $< 4\text{\AA}$ ) or the normal distances between the aromatic group and the aromatic plane of the neighboring aromatic group. All crystals were grown from slow diffusion of heptane into a THF solution.



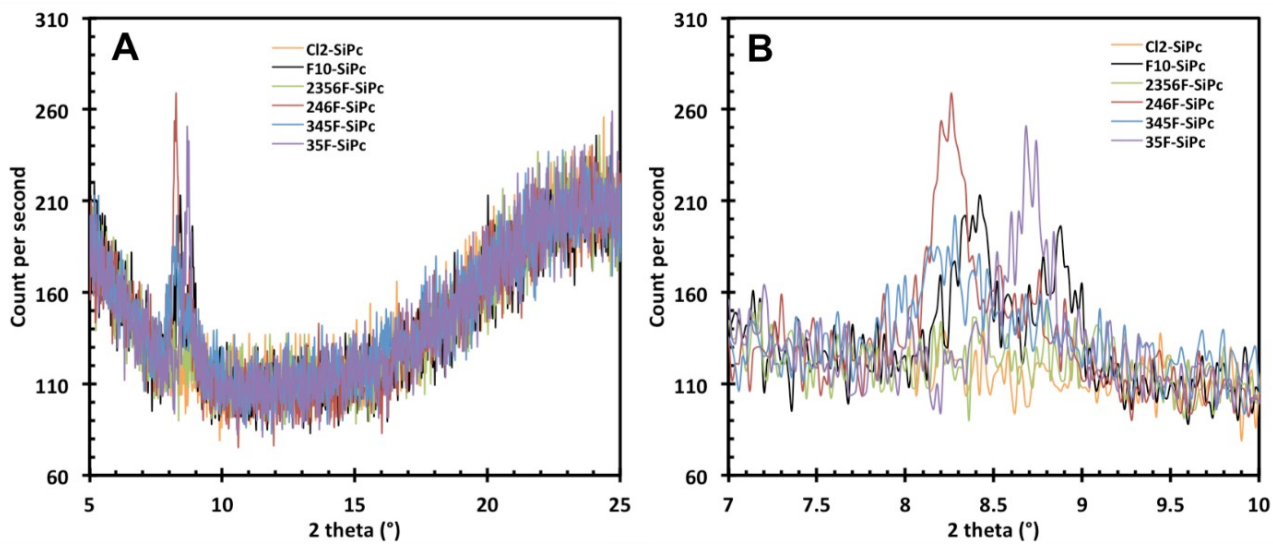
**Table S1 – Summary of Single Crystal X-ray Diffraction Data.**

Structure	Details on packing	Shortest Distance between MPc aromatic (A)	Slip angle between MPc aromatic (° / °)	Angle between aromatic planes (°)	Distance between phenoxy (A)	Slip Angle between phenoxy (° / °)	Angle between phenoxy planes (°)
Cl <sub>2</sub> -SiPc <sup>32,51</sup>	Dual benzene ring stacking	4.172, 4.172	34.87 / 36.59	1.72	-	-	-
Cl <sub>2</sub> -SiPc	Dual benzene ring stacking	3.977, 3.977	34.34 / 36.11	16.69	-	-	-
F <sub>10</sub> -SiPc <sup>32</sup>	Dual benzene ring stacking	3.769, 3.769	24.49 / 27.99	3.51	3.740	25.70 / 25.70	0
(35F) <sub>2</sub> -SiPc	Dual benzene ring stacking	3.818, 3.818	24.07 / 22.75	1.32	-	-	-
(345F) <sub>2</sub> -SiPc	Isoindoline stacking	3.716, 3.580, 3.716	18.90 / 18.90	0	-	-	-
(246F) <sub>2</sub> -SiPc	Dual benzene ring stacking	3.860, 3.860	30.08 / 30.08	0	-	-	-
(2356F) <sub>2</sub> -SiPc	Dual benzene ring stacking	3.755, 3.755	25.26 / 28.40	3.14	3.792	26.01 / 26.01	0

<sup>a)</sup>As a comparison Cl<sub>2</sub>-SiPc and F<sub>10</sub>-SiPc<sup>32</sup> were taken from the literature. All crystal structures were grown by slow diffusion of heptane into THF except Cl<sub>2</sub>-SiPc that was grown by sublimation. Slip angle between MPc aromatic = angle between centroid-to-centroid and normal of each aromatic MPc benzene. Angle between aromatic planes = smallest angle between both planes which contain the stacking aromatic benzenes

**Table S2** –X-Ray crystallographic data for for phenoxy-SiPcs

	Cl <sub>2</sub> -SiPc	F <sub>10</sub> -SiPc	(35F) <sub>2</sub> -SiPc	(345F) <sub>2</sub> -SiPc	(246F) <sub>2</sub> -SiPc	(2356F) <sub>2</sub> -SiPc
CCDC #	173621 / 148330					
Crystallization method	sublimation	Hept/THF	Hept/THF	Hept/THF	Hept/THF	Hept/THF
Empirical formula	C <sub>32</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>8</sub> Si	C <sub>44</sub> H <sub>16</sub> F <sub>10</sub> N <sub>8</sub> O <sub>2</sub> Si	C <sub>44</sub> H <sub>22</sub> F <sub>4</sub> N <sub>8</sub> O <sub>2</sub> Si	C <sub>44</sub> H <sub>20</sub> F <sub>6</sub> N <sub>8</sub> O <sub>2</sub> Si	C <sub>44</sub> H <sub>20</sub> F <sub>6</sub> N <sub>8</sub> O <sub>2</sub> Si	C <sub>44</sub> H <sub>18</sub> F <sub>8</sub> N <sub>8</sub> O <sub>2</sub> Si
Formula weight	611.52	906.74	798.78	834.77	834.77	870.75
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
a / Å	8.997(2)	8.3418(7)	8.4484(6)	10.2098(6)	9.6397(13)	8.4175(8)
b / Å	14.582(4)	10.3198(9)	13.6023(9)	17.6974(13)	19.771(3)	10.1685(9)
c / Å	10.129(4)	11.5288(10)	15.2391(10)	10.7963(7)	10.0445(10)	11.5194(10)
α / °	90	72.508(6)	90	90	90	72.562(3)
β / °	97.74	70.100(6)	97.453(3)	117.669(3)	118.661(8)	69.559(3)
γ / °	90	83.223(7)	90	90	90	81.366(3)
Unit cell volume/Å <sup>3</sup>	1316.76	889.91(13)	1736.4(2)	1727.7(2)	1679.8(4)	880.30(14)
Temperature/K	123(1)	147(2)	147(2)	147(2)	147(2)	147(2)
Space group	P 2 <sub>1</sub> /n	P -1	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /n	P 2 <sub>1</sub> /c	P -1
No. of formula units per unit cell, Z	2	1	2	2	2	1
ρ <sub>calc</sub> / Mg/m <sup>3</sup>	1.542	1.692	1.528	1.605	1.650	1.643
Absorption coefficient / mm <sup>-1</sup>	0.334	1.563	1.258	1.380	1.419	1.467
No. of reflections measured	12793	14965	11884	11544	9308	11039
No. of independent reflections	2689	2951	2992	2962	2847	2991
R <sub>int</sub>	0.0420	0.0625	0.0238	0.0273	0.0817	0.0210
Final R <sub>1</sub> values (I > 2σ(I))	0.0395	0.0681	0.0301	0.0321	0.0657	0.0311
Final wR(F <sup>2</sup> ) values (I > 2σ(I))	0.0943	0.1826	0.0767	0.0819	0.1583	0.0819
Final R <sub>1</sub> values (all data)	-	0.0858	0.0335	0.0372	0.0991	0.0317
Final wR(F <sup>2</sup> ) values (all data)	-	0.1930	0.0792	0.0850	0.1755	0.0825



**Figure S8** -Powder X-ray crystallography (XRD) diffractions of thin films (50 -70 nm) of / $(XF)_2$ -SiPc on glass substrates from (A)  $2\theta = 5 - 25^\circ$  and (B)  $2\theta = 7 - 10^\circ$ .

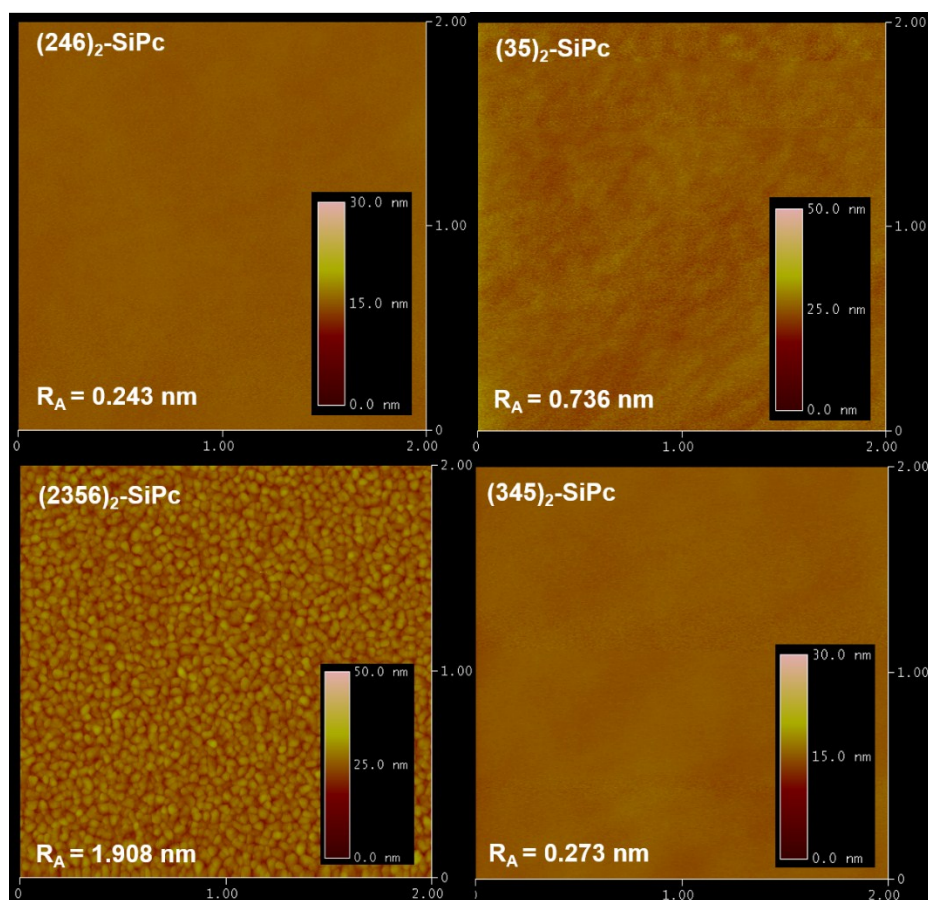
**Table S3.** Powder XRD characterization of thin films of (XF)<sub>2</sub>-SiPc obtained by thermal evaporation.

Sample	Predicted XRD <sup>a)</sup>		Experimental XRD <sup>b)</sup>			Ref.
	2θ (°)	d spacing <sup>c)</sup> (Å)	2θ (°)	d spacing <sup>c)</sup> (Å)	Max Intensity (Counts·s <sup>-1</sup> )	
Cl <sub>2</sub> -SiPc	10.60	8.3	-	-	137	<sup>32</sup>
F <sub>10</sub> -SiPc	8.48	10.4	8.42	10.5	213	<sup>32</sup>
(2356F) <sub>2</sub> -SiPc	8.48	10.4	8.80	10.0	154	This work
(246F) <sub>2</sub> -SiPc	8.94	9.9	8.26	10.7	269	This work
(345F) <sub>2</sub> -SiPc	9.86	9.0	8.28	10.7	202	This work
(35F) <sub>2</sub> -SiPc	8.74	10.1	8.68	10.2	250	This work

<sup>a)</sup> Powder XRD, 2θ values predicted from single crystal X-ray diffractions.

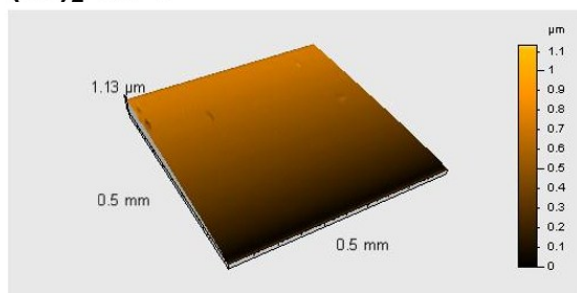
<sup>b)</sup> Experimental powder XRD were determined on thin films (50-70 nm) of SiPc deposited by thermal evaporation onto a glass slide.

<sup>c)</sup> d spacing calculated from Bragg's law ( $d = \lambda / (2 \cdot \sin(\theta))$ ), using  $\lambda = 1.54 \text{ \AA}$



**Figure S9** – Atomic Force microscopy performed on thermally evaporated thin films (40-50 nm ) of  $(246)_2$ -SiPc (Top left),  $(35)_2$ -SiPc (Top right),  $(2356)_2$ -SiPc (bottom left) and  $(345)_2$ -SiPc (bottom right) on glass. In all cases the samples were analyzed using tapping mode and the characteristic images in this Figure are of a sample size  $2 \times 2 \mu\text{m}$ . The inset is a depth colour scale to show the range of distances between peak to valley. Average roughness ( $R_A$ ) for each sample is also included in the respective figure.

### (35)<sub>2</sub>-SiPc



Parameters calculated on the surface  
Unknown > ... > Levelled (LS)

Sz, Sds and Ssc parameters are defined according to EUR15178N report.

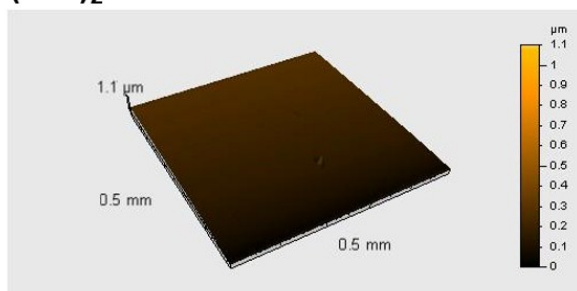
Amplitude Parameters

Sa	= 0.024 μm
Sq	= 0.031 μm
Sp	= 0.411 μm
Sv	= 0.134 μm
St	= 0.546 μm
Ssk	= -0.81
Sku	= 8.17
Sz	= 0.319 μm

Functional Parameters, Gaussian Filter, 0.128 nm

Sk	= 0.00624 μm
Spk	= 0.00564 μm
Svk	= 0.015 μm

### (246)<sub>2</sub>-SiPc



Parameters calculated on the surface  
Unknown > ... > Levelled (LS)

Sz, Sds and Ssc parameters are defined according to EUR15178N report.

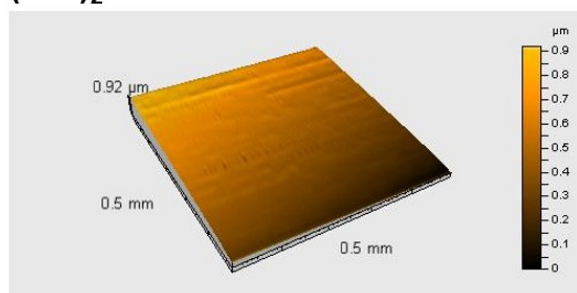
Amplitude Parameters

Sa	= 0.0127 μm
Sq	= 0.0204 μm
Sp	= 0.943 μm
Sv	= 0.0809 μm
St	= 1.02 μm
Ssk	= 11.1
Sku	= 504
Sz	= 0.31 μm

Functional Parameters, Gaussian Filter, 0.128 nm

Sk	= 0.00544 μm
Spk	= 0.00548 μm
Svk	= 0.0101 μm

### (345)<sub>2</sub>-SiPc



Parameters calculated on the surface  
Unknown > ... > Levelled (LS)

Sz, Sds and Ssc parameters are defined according to EUR15178N report.

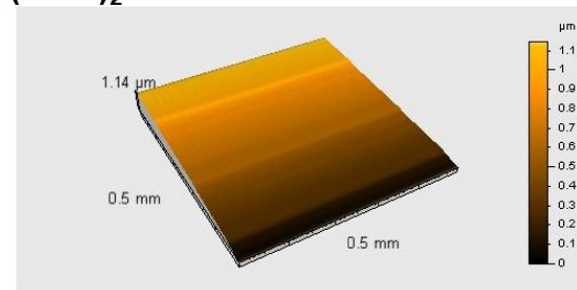
Amplitude Parameters

Sa	= 18.8 nm
Sq	= 25.5 nm
Sp	= 136 nm
Sv	= 97 nm
St	= 233 nm
Ssk	= -0.617
Sku	= 5.74
Sz	= 176 nm

Functional Parameters, Gaussian Filter, 0.128 nm

Sk	= 14.6 nm
Spk	= 16.1 nm
Svk	= 16 nm

### (2356)<sub>2</sub>-SiPc



Parameters calculated on the surface  
Unknown > ... > Levelled (LS)

Sz, Sds and Ssc parameters are defined according to EUR15178N report.

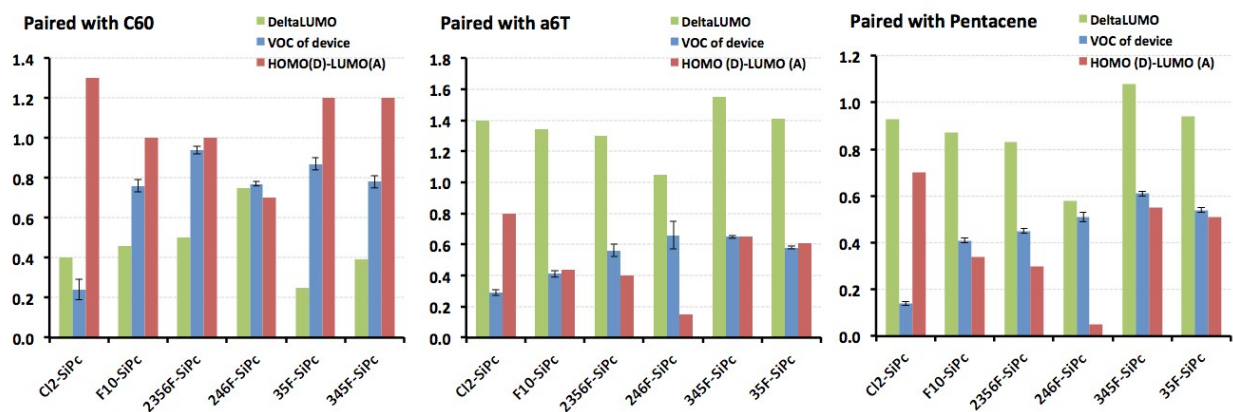
Amplitude Parameters

Sa	= 25.9 nm
Sq	= 35.3 nm
Sp	= 137 nm
Sv	= 133 nm
St	= 270 nm
Ssk	= -1.24
Sku	= 5
Sz	= 175 nm

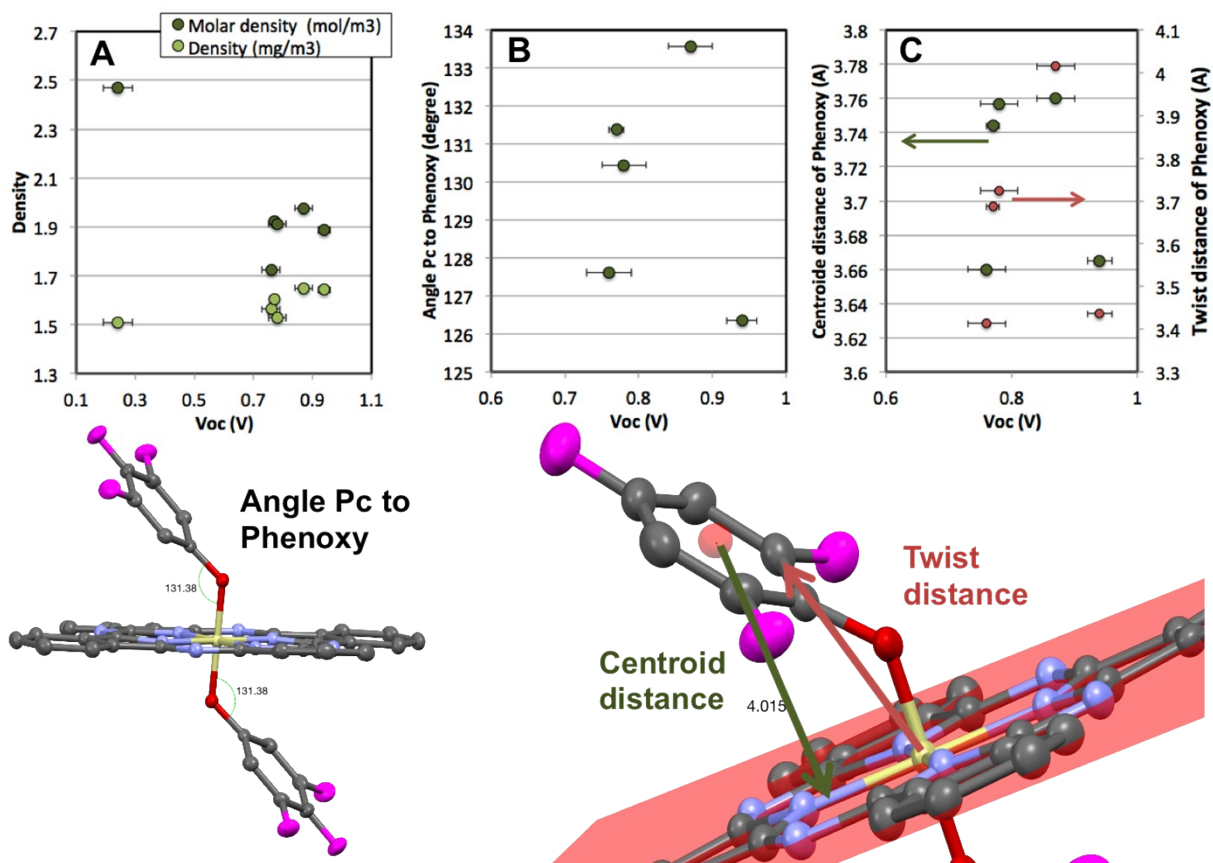
Functional Parameters, Gaussian Filter, 0.128 nm

Sk	= 15.5 nm
Spk	= 25.4 nm
Svk	= 23.2 nm

**Figure S10** – Stylus Profilometry performed on thermally evaporated thin films (40-50 nm ) of (246)<sub>2</sub>-SiPc, (35)<sub>2</sub>-SiPc, (2356)<sub>2</sub>-SiPc and (345)<sub>2</sub>-SiPc on glass. In all cases the sample size 0.5 x 0.5 mm. The tables (right) correspond to the values obtained from the respective surfaces (left).

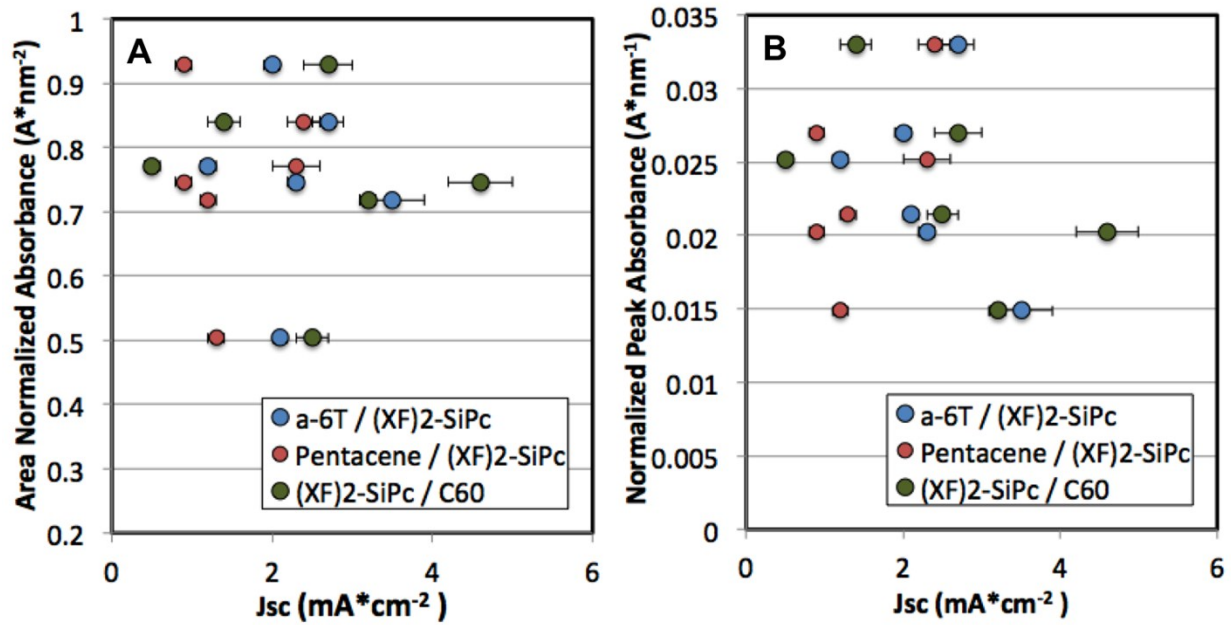


**Figure S11 – Device  $V_{OC}$ , calculated  $I_g \approx \text{HOMO (donor layer) - LUMO (acceptor layer)}$  and calculated delta = LUMO (acceptor layer) - LUMO (donor layer) for all SiPc containing devices found in **Table 3**.**



**Figure S12** – Single crystal X-ray diffraction characteristics versus obtained **Device**  $V_{OC}$ . A) Density versus obtained **Device**  $V_{OC}$ . B) Angle of phenoxy versus obtained **Device**  $V_{OC}$  (as depicted in bottom left of figure). C) Distance from the Pc plane to the centroide and the distance from the Si molecule and the furthest carbon on the phenoxy versus obtained **Device**  $V_{OC}$  (as depicted in bottom right of figure).





**Figure S13** – A) Area and B) max peak height of thickness-normalized absorbance versus obtained Device  $J_{sc}$ . All SiPc containing PHJ OPV devices characteristics found in Table 3.