Supporting Information: Synthesized Ligands of Amino Phenyl TIPS-pentacene and Tetraphenylporphyrin for Singlet Fission

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1 Molecules' Shape and Configurations

Ligands like tetraphenylporphyrin (H_2TPP) and zinc tetraphenylporphyrin (Zn-TPP) were purchased commercially. Afterwards, mono- and di- carboxylic acid side groups have been added to these molecules by Prof. Marcus Scheele's group at the university of Tübingen to shield and cross link the PbS nanoparticles. Molecules can take several configurations in the real space. Using jaguar simulation tool, which is a powerful tool for ab-initio quantum chemistry allow us to measure the angles among the phenyl rings. Figure 1 shows no angle (0°) among the phenyl rings of H_2-TPP which are attached to one carboxyl side group (COOH). Figure 2 shows a constant angle (50°) between each two corresponding phenyl rings which are labeled (1-3) and (2-4) in table 1. The inner phenyl rings number 3´ and 4´ changed their positions in connection to the outer rings to be 0.1° because of adding large zinc atoms. This change leads phenyl rings labeled 1 and 3 to form (+50.1°) and (-0.1°) angles with reference to the molecule main backbone. Here, it is necessary to mention that the reacted terminal attached to phenyl ring labeled with number 1 elongates the molecule

from 17.53 A° to 19.38 A°. Further more, molecules may change in length and angles after their reaction with PbS to reach the stability in final COINS form. The two carboxyl side groups are used to cross link the QDs. They in turn increase the length of Zn-TPP molecule from (17.53 A°) to (21.27 A°) long axis if we consider the active reaction ends of molecule terminals (COO^{-}) without H^{+} proton. The angle between inner rings labeled with 2´ and 4´ is found to be zero. The outer rings again modify their positions with respect to the main molecule backbone to (-0.1°) and (+50.1°).

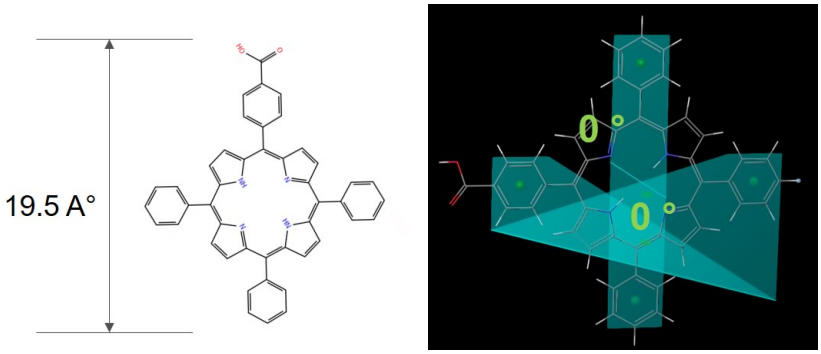


Figure 1: m-H_2TPP molecule configurations with one carboxylic acid side group (COOH): dimensions and angles.

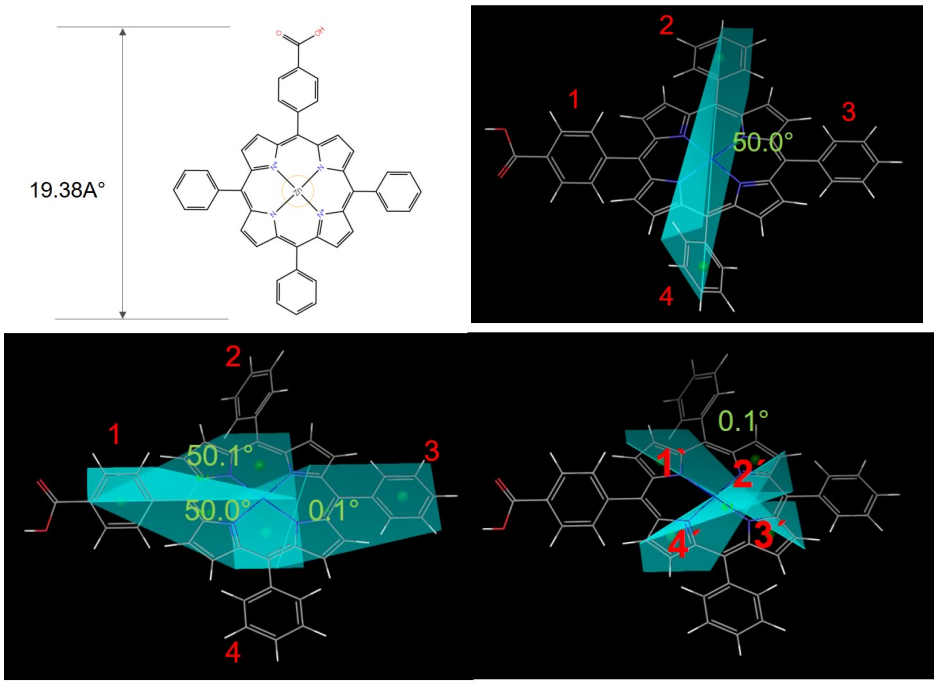


Figure 2: m-Zn-TPP molecule configurations with one carboxylic acid side group (COOH): dimensions and angles.

Table 1: List of dimensions and angles for m-Zn-TPP molecule configurations with one carboxylic acid side group (COOH).

terminals	length (A°)	angle (deg)
1-3	19.38	50
2-4	17.53	50
1-backbone		+50.1
3-backbone		-0.1

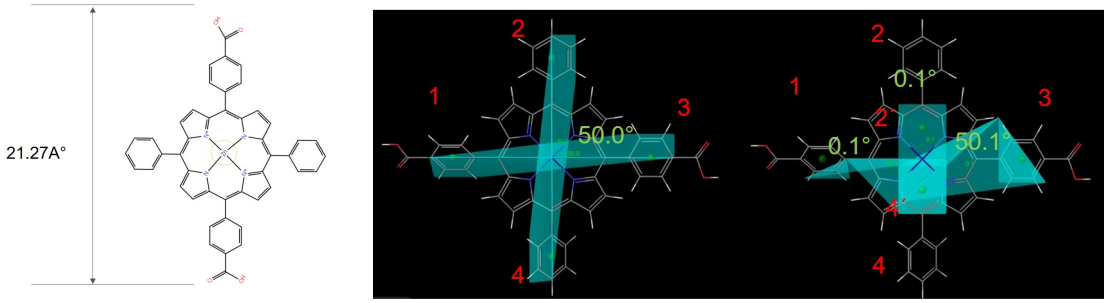


Figure 3: di-Zn-TPP molecule configurations with two carboxylice acid side group (2COOH): dimensions and angles.

Table 2: List of dimensions and angles for di-Zn-TPP molecule configurations with two carboxylic acid side group (2COOH)

terminals	length (A°)	angle (deg)
1-3	21.27	50
2-4	17.53	50
1-backbone		+50.1
3-backbone		-0.1
2´-4´		0.1

2 TEM, FFT and Live Profile for PbS- Ligands

In connection to the manuscript results, we measured the interparticle distances for different PbS-ligands from the real images of scanning transmission electron microscope (STEM) and their fast Fourier transformation (FFT). Another option would be measuring these spaces using the same GATAN software and measuring the live profile by applying a straight line for several adjacent NCs. Figure 4 (a) exposes the PbS-OA image. It highlighted the first monolayer which has an ordered hexagonal lattice. The inter-particles' voids which are obtained from the real, FFT and live profile are given in Table 3. Inverted FFT could be used precisely to determine the distances of the live profile after applying a mask to selective bright diffraction spots. The histogram of PbS nanopartcile normalized size distribution is illustrated in Figure 4.

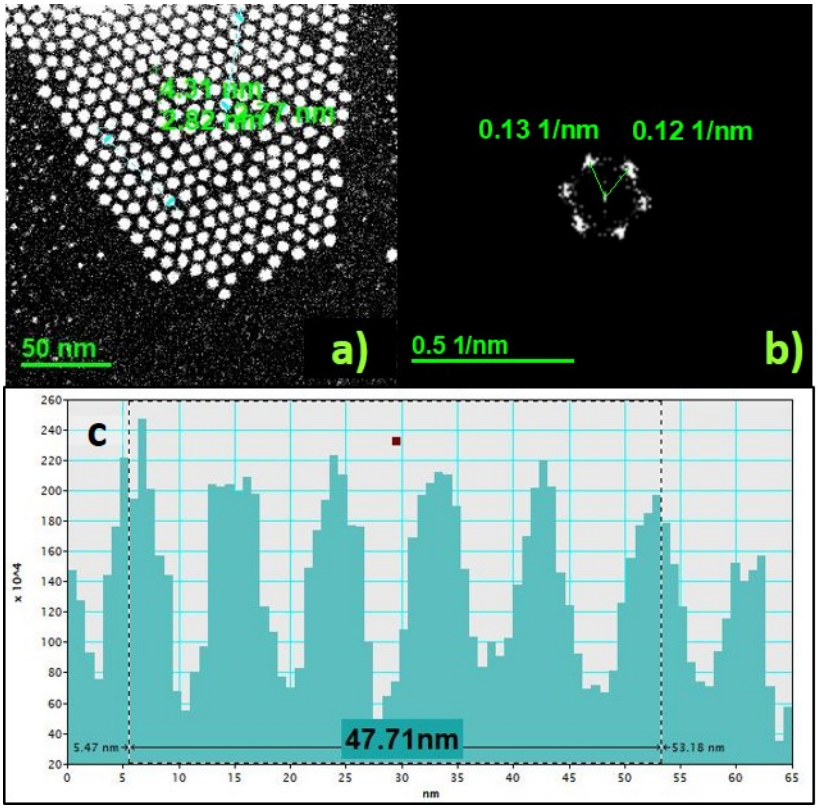


Figure 4: TEM images for PbS-NCs capped with a) oleic acid, b) FFT for region 1 c) FFT for region 2 d) live profile for the first monolayer and e) second monolayer.

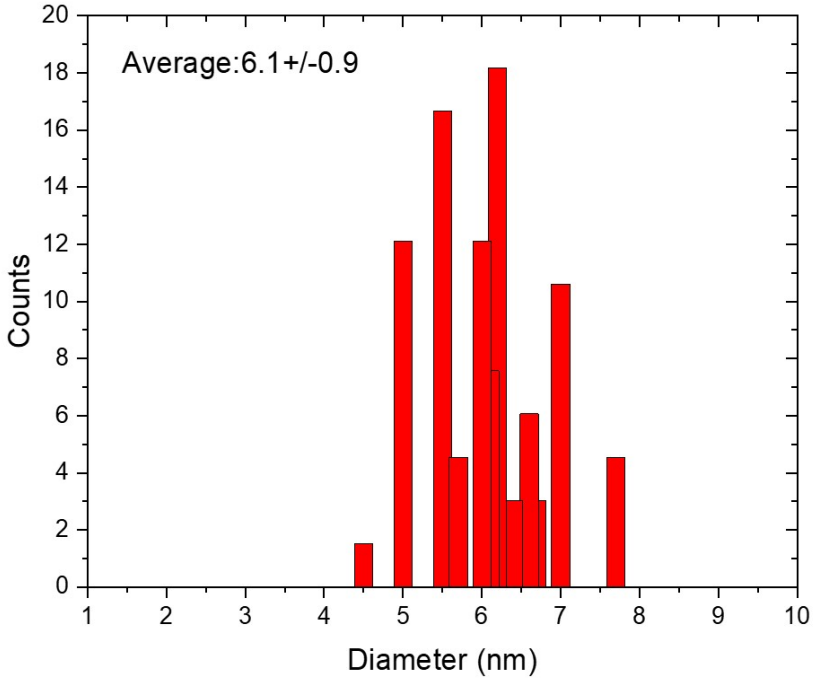


Figure 5: Corresponding normalized size distribution histogram of native OA-capped PbS NCs

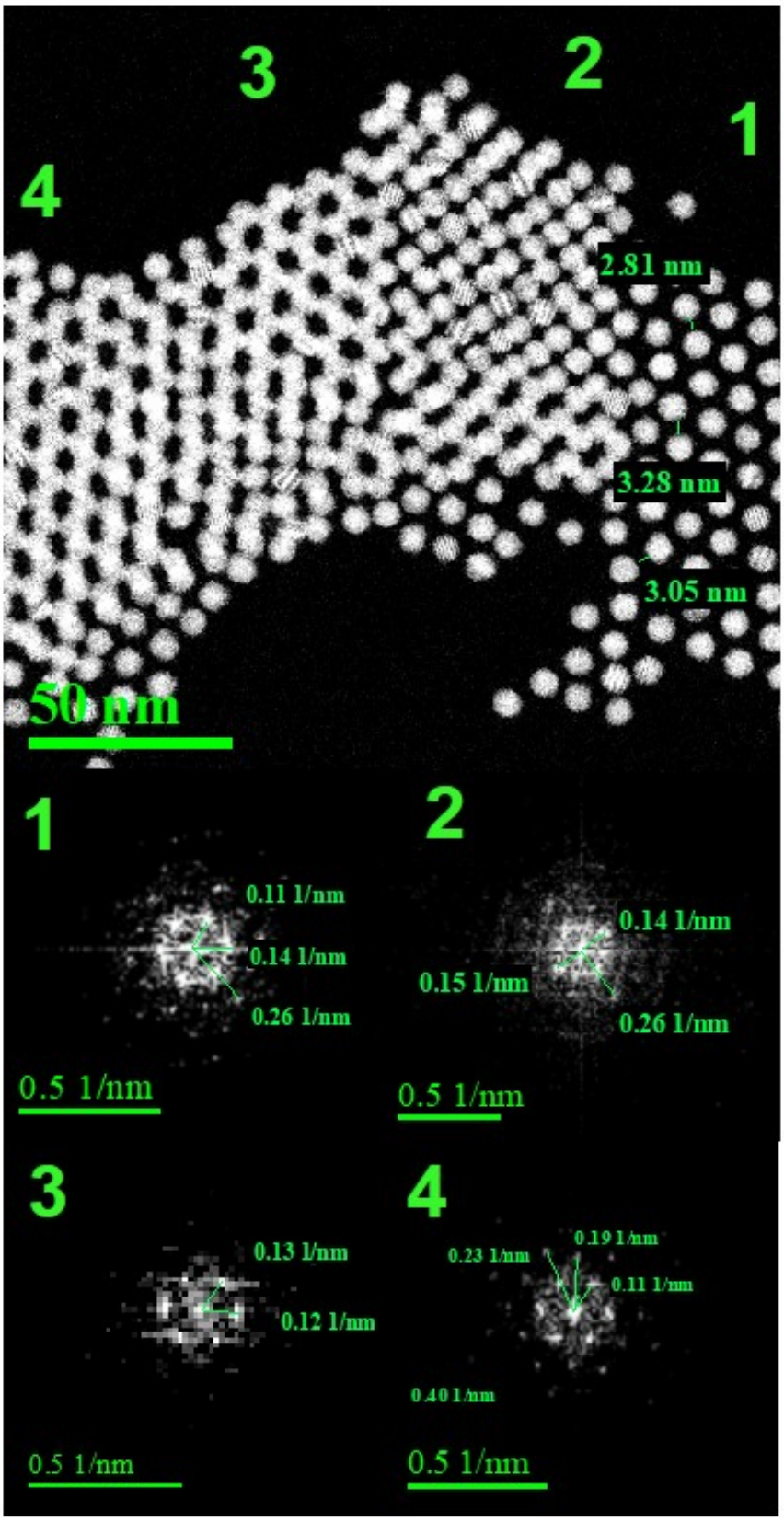


Figure 6: STEM and FFT images of PbS-AP-TIPs-pentacene.

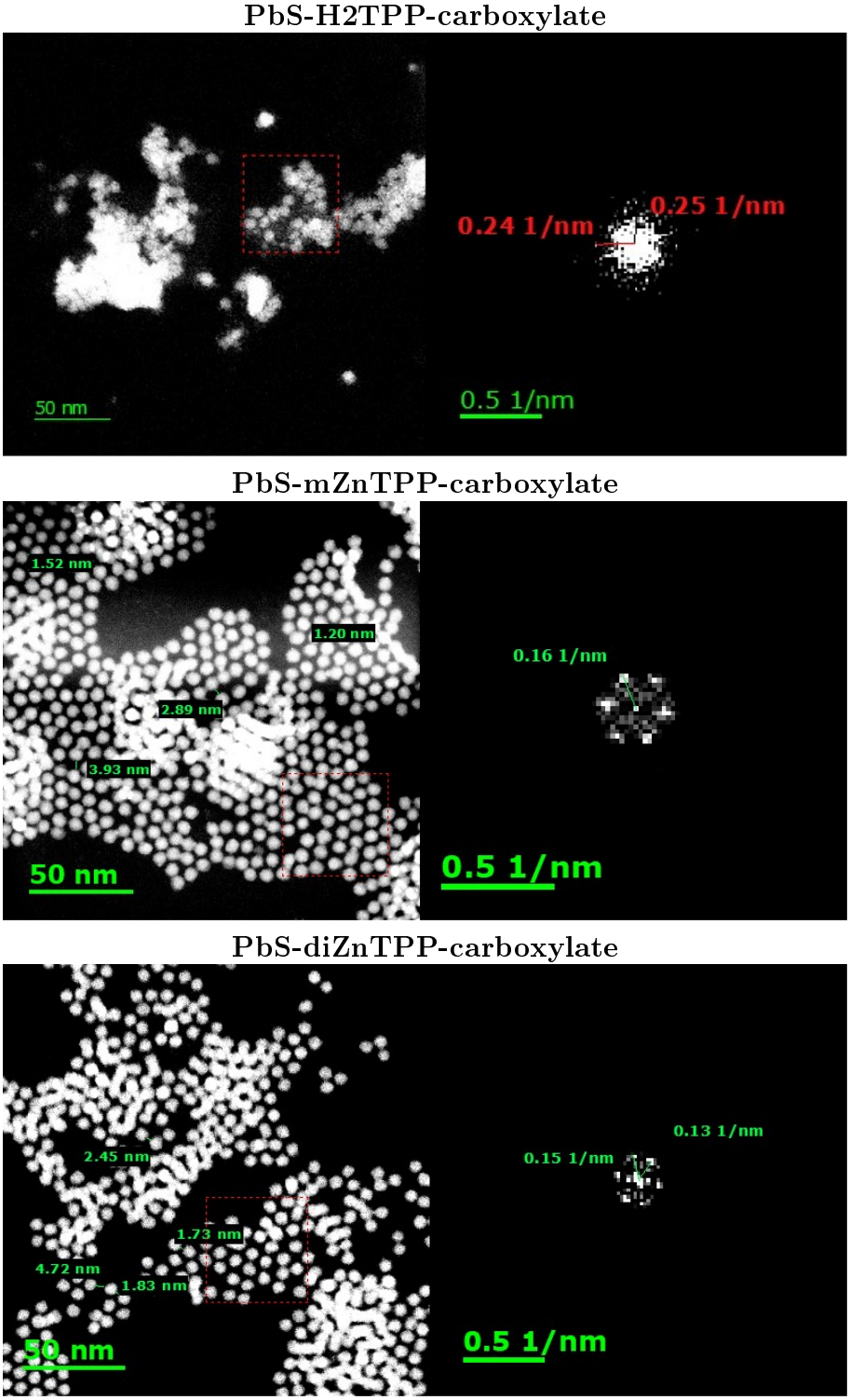


Figure 7: STEM and FFT images of mono- and diZnTPP-carboxylate.

Table 3: List of interparticles' distances of different ligands.

$d_{\text{real image}}$	FFT	$d_{1/\text{FFT}}$	$d_{\text{live profile}}$
(nm)	(1/nm)(no. domain)	(nm)	(nm)
PbS-OA			
2.77	0.12	2.23	1.48
2.82	0.13	1.59	3.44
4.31			
PbS-AP-TIPs-pentacene			
2.81	0.11(1,4)	2.99	3.40
3.28	0.12(3)	2.23	
3.05	0.13(3)	1.59	
	0.14(1,2)	1.04	
	0.15(2)	0.57	
PbS-H2TPP-carboxylate			
0.92	0.13	1.59	1.07
2.03	0.15	0.57	
PbS-mZnTPP-carboxylate			
1.2	0.16	0.15	1.66
1.52			
2.8			
3.93			
PbS-diZnTPP-carboxylate			
1.73	0.13	1.59	2.15
1.83	0.15	0.57	
2.45			
4.72			

3 Atomic Resolution

It is important to mention that samples for TEM are prepared by dip-coating on carbon substrates. Atomic resolution can be analyzed from the real images of TEM or their FFT for PbS-AP-TIPs- pentacene (figure 8). These NCs have different lattice planes which can be estimated from GATAN program simulation. The lattice constant value is (5.9894A°) for large size NCs.[1] The dominant planes are (111) and (100) for cuboctahedron crystallographic structure which is the typical unit cell for such large nanoparticles, FFT diffraction patterns depict more lattice planes like (300), (220) and (222) and etc. There are some values of

inverse FFT lying between two lattice planes. This can be explained either because of software approximation or some planes receive dislocation in the same nanocrystal structure. In this work, several ligands (Figure 10 and 11) have been equitably analyzed in their planes for PbS NCs. There is no idiosyncrasy in term of preferable lattice planes reaction towards different ligands. Several lattice planes of (111), (200), (220), and (400) have been resolved from the FFT of these spot areas.

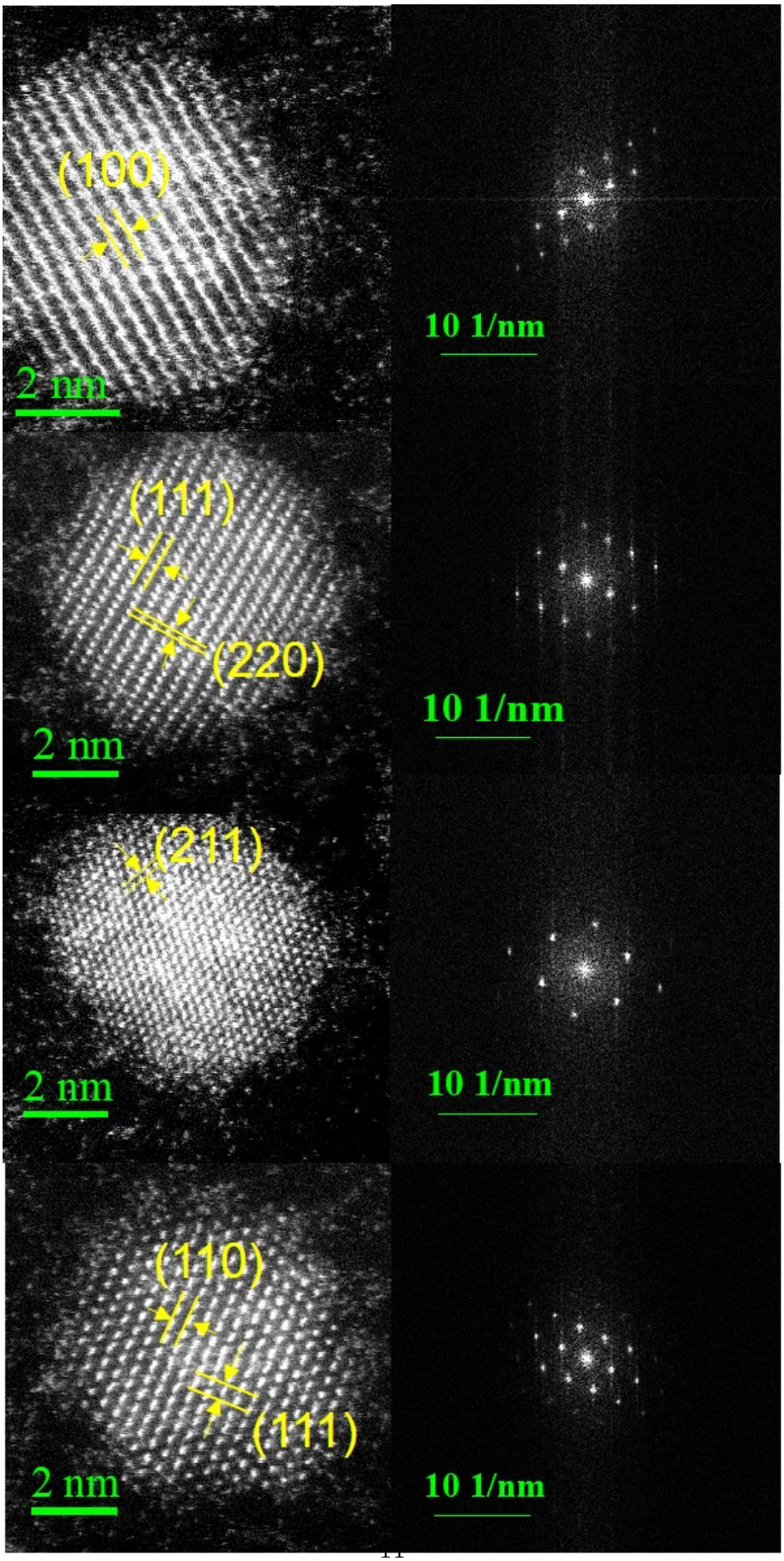


Figure 8: Atomic resolution of PbS nanoparticles with AP-TIPs-pentacene ligand.

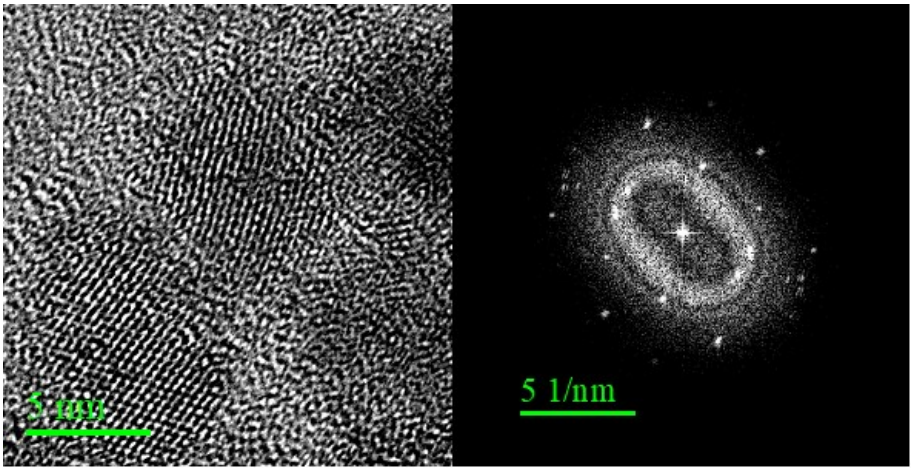


Figure 9: Atomic resolution of PbS nanoparticles with H2TPP-carboxylate ligand.

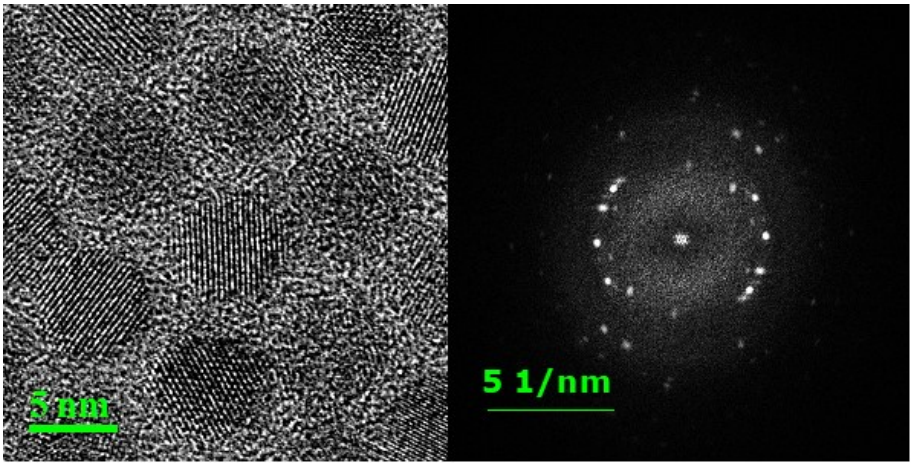


Figure 10: Atomic resolution of PbS nanoparticles with mZnTPP-carboxylate ligand.

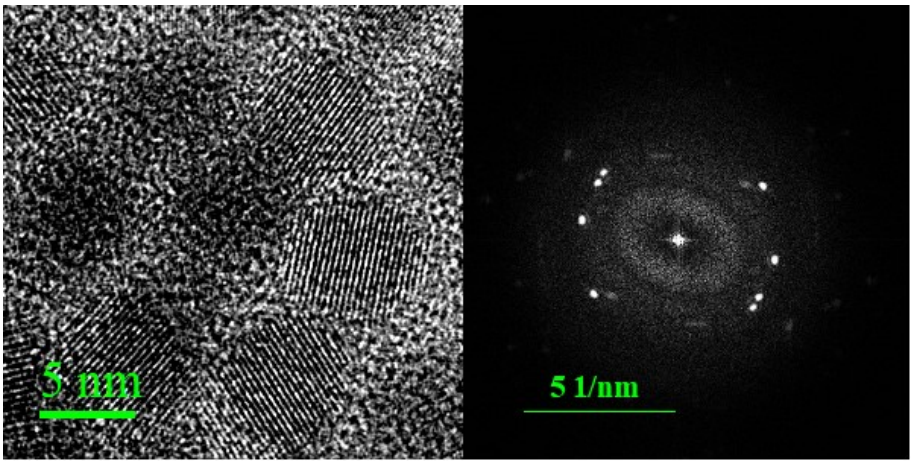


Figure 11: Atomic resolution of PbS nanoparticles with diZnTPP-carboxylate ligand.

4 Effective Dielectric Constant

The effective dielectric constanst of COINS with variant ligands were calculated according to Maxwell-Garnett effective media theory (1):[2]

$$\epsilon_{eff} = \epsilon_m \frac{\epsilon_{np}(1+2\theta) - 2\epsilon_m(\theta - 1)}{\epsilon_m(2+\theta) + \epsilon_{np}(1-\theta)}\,, \tag{1}$$

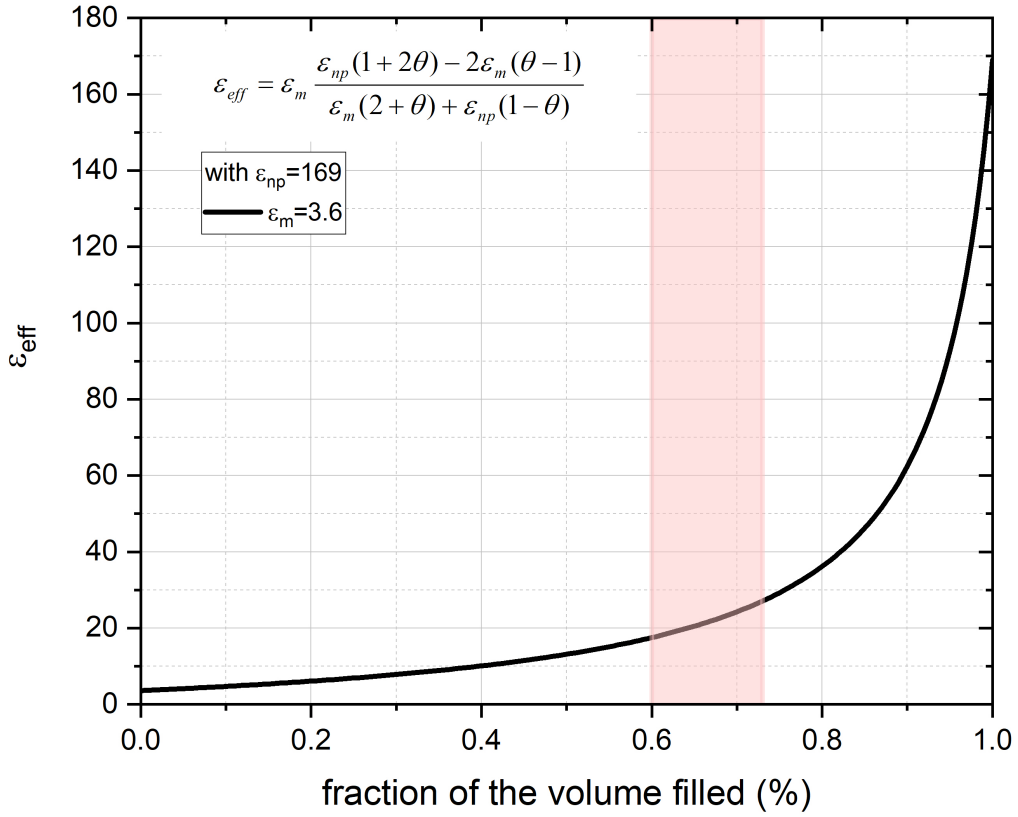
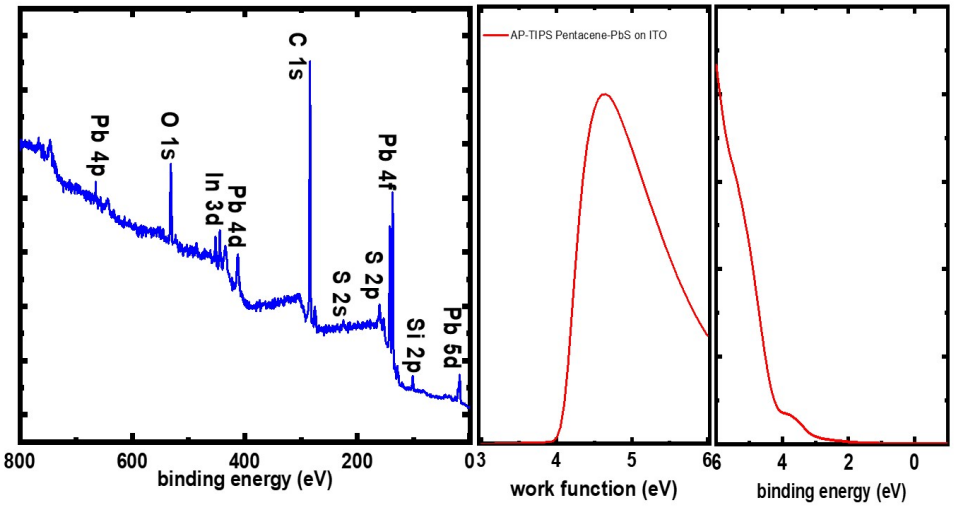


Figure 12: Effective dielectric constant for PbS-AP-TIPs-Pentacene.

The PbS-QDS with the new ligand AP-TIPs-pentacene form a hexagonal unit cell in their propagation. Figure 12 reveals two values of effective dielectric constant for PbS-AP-TIPs-pentacene with two different filling factors of 0.6 and 0.74 when we assumed two different hexagonal unit cells. The first value (0.6) corresponds to an extra layer added at the middle of the side height of the unit cell and the second (0.74) corresponds to the normal hexagonal unit cell. The first assumption was considered in the main manuscript for capacitance calculations. The dielectric constant is (17.53) when the volume fraction is 0.6.

5 Energy Levels, UPS and XPS

1. AP-TIPs-pentacene



2. H2TPP

3. mZnTPP

4. diZnTPP

References

(1) Beygi, H.; Sajjadi, S. A.; Babakhani, A.; Young, J. F.; van Veggel, F. C. Surface chemistry of as-synthesized and air-oxidized PbS quantum dots. *Applied Surface Science* **2018**, *457*, 1–10.

(2) Scheele, M.; Engel, J. H.; Ferry, V. E.; Hanifi, D.; Liu, Y.; Alivisatos, A. P. Nonmonotonic size dependence in the hole mobility of methoxide-stabilized PbSe quantum dot solids. *ACS nano* **2013**, *7*, 6774–6781.