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## Monofluorination of Naphthyls Promotes the Cofacial $\pi-\pi$ Stacking and Increases the Electron Mobility of Non-Planar Zinc(II) Complexes of Di(naphthylethynyl)azadipyrromethene

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revealed cofacial parallel-displaced  $\pi-\pi$  stacking between the fluorinated 1-naphthylethynyl groups. Such a cofacial orientation was not observed in  $Zn(L2)_2$  crystals, suggesting that fluorination of the naphthyl groups promotes the cofacial  $\pi - \pi$  stacking orientation. The hole mobility increased from  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for Zn(L2)<sub>2</sub> to  $0.8 - 1.0 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the fluorinated complexes. Fluorination on the naphthyl groups increased the electron mobility from  $4.2 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for Zn(L2)<sub>2</sub> and  $Zn(1F-L2)_2$  to  $2.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$ , consistent with cofacial  $\pi-\pi$  stacking being favorable for electron transport. The three complexes were tested in OPVs using regioregular poly(3-hexylthiophene) (P3HT) as the p-type material, and the best power conversion efficiencies were 5.2, 5.4, and 5.8% for Zn(2F-L2)<sub>2</sub>, Zn(1F-L2)<sub>2</sub>, and Zn(3F-L2)<sub>2</sub>, respectively, compared to 5.5% for  $Zn(L2)_2$ . The fluorination combination found in  $Zn(3F-L2)_2$  resulted in the best device performance. This study points to a viable strategy to increase the electron mobility and performance of non-planar zinc(II) complexes of azadipyrromethene.

## INTRODUCTION

Solution-processable semiconductors are of great interest because they can be printed at low temperatures to give lightweight, bendable, and low-cost electronic devices such as photovoltaics, displays, transistors, flexible displays, disposable sensors, and smart packaging.<sup>1-4</sup> The development of organic semiconductors, in conjunction with device optimization, has propelled organic photovoltaic power conversion efficiencies (PCEs) from about 4% for the first successful and well-studied P3HT/PC<sub>61</sub>BM system to ~12% for fullerene-based OPVs, where the conjugated polymer donor is optimized for a fullerene-derivative electron acceptor such as PC71BM, and to over 17% for non-fullerene-based OPVs and ternary OPVs.<sup>5–10</sup> As PCEs increase, research is shifting to other aspects that are required for commercialization of OPVs, including the stability and cost.<sup>11–13</sup> Most highly efficient OPVs currently use expensive active layer materials, such as donor-acceptor conjugated polymer electron donors and fused-ring electron acceptors, that have very high synthetic complexity.<sup>14,15</sup> A recent

on both  $[Zn(3F-L2)_2]$  were synthesized and characterized. All

three complexes had similar optical and electrochemical properties. The crystal packing structure of  $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$ 

> study predicts that OPVs can reach nearly 20% efficiency and that the efficiency depends more on the electron acceptor optoelectronic properties than those of the electron donor.<sup>12</sup> If that is the case, then it makes sense to develop electron acceptors that work well with inexpensive polythiophene-based conjugated polymer donors such as P3HT. The recent development of non-fullerene acceptors (NFAs) to be paired with simple polythiophene-based donors has shown great promise, with PCEs now exceeding 10%.<sup>16</sup> Successful NFAs tend to fall into two general categories: fused-ring planar conjugated systems with bulky side chains and a non-planar conjugated system

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X=H, Zn(2F-L2)<sub>2</sub> X=F, Zn(3F-L2)<sub>2</sub>





typically consisting of two or more planar molecules such as perylene diimides connected by some organic bridge.<sup>17–20</sup> Most are conjugated organic materials, where their optoelectronic properties are typically tuned with the nature of the chemical backbone, functional groups, and side chains. Non-covalent intramolecular interactions have also been used to planarize conjugated systems and were recently used in the design of planar NFAs with similar performance as fused-ring NFAs, but with lower synthetic complexity.<sup>21–24</sup>

A much less-explored type of NFA is hybrid organic/ inorganic coordination compounds, where the coordination with a main group element or transition metal provides an additional way to tune properties such as the molecular shape, crystallinity, and optoelectronic properties. Examples in the literature of coordination complexes specifically explored for organic photovoltaic applications include porphyrins and phthalocynanines,<sup>25–28</sup> which are planar with a strong tendency to  $\pi$ -stack; boron dipyrromethenes (BODIPY) and boron azadipyrromethenes (aza-BODIPY),<sup>29–32</sup> which are also planar conjugated molecules better known for their outstanding optical properties; and subphthalocynanines, which are umbrella-shaped conjugated molecules.<sup>33,34</sup>

We have pioneered homoleptic zinc(II) complexes of azadipyrromethene as non-planar NFAs for organic photovoltaic applications.<sup>35</sup> Azadipyrromethenes are  $\pi$ -conjugated bidentate ligands that have strong absorption in the visible to near infrared (NIR) range, good fluorescence properties, and high electron affinity.<sup>36,37</sup> The easiest ligand to synthesize is 1,3,7,9-tetraphenyl-azadipyrromethene (ADP), shown in Figure 1. ADPs are typically coordinated with difluoroboryl (BF<sub>2</sub>),



Figure 1. ADP,  $Zn(WS3)_2$ , and  $Zn(L2)_2$ .

known as aza-BODIPY, but they can also be coordinated with other group 13 elements and transition metals.<sup>36,38</sup> In these molecules, the zinc(II) transition metal's function is to hold the two ADP ligands together in a distorted tetrahedral geometry, with intramolecular  $\pi - \pi$  stacking in four places between the proximal phenyls of one ligand and the pyrroles of the other ligand, leading to rigid and fully conjugated non-planar molecules with high electron affinity and low reorganization energy.<sup>39,40</sup> Phenylethynyl groups at the pyrrolic positions extend the conjugated system, broadening the absorption spectra to about 800 nm. In looking for an appropriate electron donor, we selected P3HT not only because it is cheap and readily available but also because its absorption spectrum complements that of the zinc complexes, and its energy levels are appropriate to facilitate charge separation. P3HT:Zn(WS3)<sub>2</sub> solar cells showed PCEs of up to ~4%.<sup>35,41</sup>

Recently, we reported a zinc(II) complex of di-(naphthylethynyl)azadipyrromethene  $[Zn(L2)_2]$ , where the phenyls in the pyrrolic groups were replaced with 1-naphthyl and hexyl solubilizing groups were added to the proximal phenyls. These molecular changes increased the crystallinity, charge carrier mobility, and OPV performance, reaching a PCE as high as 5.5% when blended with P3HT.<sup>42</sup> This complex also has a low synthetic complexity of only 22.1%, increasing its industrial accessibility. The hole mobility of  $Zn(L2)_2$  in neat films is adequate for OPVs at  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [estimated by the space charge-limited current (SCLC) method]. However, the electron mobility is low at  $4.2 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which may limit its performance in devices. The extent of molecular overlap (or overlap integrals) was estimated for pairs of adjacent molecules from the packing structure and is also low, consistent with low mobilities. This is partly because of the non-planar geometry of  $Zn(L2)_2$  and partly because the protruding groups are all non-polar unsubstituted aryls, which typically prefer the T-shaped edge-to-face orientation. 43-45 Interestingly, while Tshaped interactions are good for hole transport, they are not optimal for electron transport; cofacial orientation is better for electron transport.46,47 To increase the electron mobility of  $Zn(L2)_2$ , we thus looked for chemical structure modifications that promote stronger cofacial intermolecular  $\pi - \pi$  stacking interactions.

Common ways to control molecular packing and promote  $\pi - \pi$  stacking interactions of planar  $\pi$ -conjugated compounds include heteroatom substitution in the  $\pi$ -conjugated system, substitution in the periphery of the conjugated system, strategic choice and position of solubilizing groups, and promotion of  $\pi$ conjugated planarity.48,49 In particular, fluorine substitution has been widely investigated to tune the properties of conjugated systems, including crystal packing.<sup>48,50–53</sup> The fluorine atom has a high electronegativity, which can affect the energy levels and introduce local dipole moments, and is small, meaning that it can influence properties without increasing steric effects. 50,54 In the case of the simplest aromatic interaction, the benzene dimers tend to prefer T-shaped (edge-to-face) interactions,<sup>55</sup> though calculations indicate that parallel-displaced (cofacial but shifted) interactions are nearly isoenergetic with the T-shaped configuration.<sup>56</sup> The addition of substituents on one of the benzene rings increases the attractive interactions of the benzene-substituted benzene dimer with the sandwich (cofacial) configuration.<sup>56-58</sup> Dunietz and co-workers computationally demonstrated how selective fluorination of naphthalene can enhance the intermolecular interaction, promote cofacial  $\pi - \pi$ stacking with C-F pointing in opposite directions to minimize the local dipole, and increase the mobility.<sup>59</sup> Ichikawa and coworkers synthesized singly fluorinated phenacenes and showed the fluorine-induced polarization. The crystal structure showed intermolecular C-H…F interactions and the dimers formed face-to-face stacks (C-F bonds pointing in the opposite direction) rather than the typical T-shaped configuration, demonstrating that single fluorination is enough to promote face-to-face stacking in larger fused benzene-ring systems.<sup>60</sup> Chung, Son, and co-workers prepared a series of alternating D-

A molecular semiconductors based on  $7,7'-(4,4-bis(2-ethyl-hexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(4-(5'-hexyl-[2,2'-bithiophene]-5-yl)benzo[c][1,2,5]thiadiazole) with different fluorine substitution patterns.<sup>61</sup> The number and location of fluorines on the benzothiadiazole unit strongly influenced the molecular packing, charge transport, and photovoltaic properties. Interestingly, the best performances were obtained for the molecules with symmetric and even number of fluorines, which allowed the formation of well-defined <math>\pi-\pi$  stacking interactions, where the molecules organize themselves to minimize the net dipole moment.

There is not much known about using fluorination to increase the  $\pi-\pi$  stacking interactions in non-planar coordination compounds such as our zinc complexes. We have previously found that fluorination of Zn(WS3)<sub>2</sub> either at the distal phenyl or at the pyrrolic phenylethynyls increases the electron mobility in neat films,<sup>41</sup> but only limited information about intermolecular  $\pi-\pi$  interactions was obtained because most complexes did not form resolvable single crystals. Single-crystal X-ray diffraction is essential to gain insights about film morphology and intrinsic charge transport properties.<sup>62</sup> Zn(L2)<sub>2</sub>, on the other hand, can easily be crystallized due to the hexyl solubilizing groups and the larger aryl group on the pyrrolic substituents,<sup>42,43</sup> making it a better platform to study the influence of fluorination of intermolecular interactions in non-planar  $\pi$ -conjugated systems. In this work, we explored the fluorination of Zn(L2)<sub>2</sub> (Figure 2) at the distal phenyls [Zn(1F-L2)<sub>2</sub>], proximal 1-



**Figure 2.** New fluorinated  $Zn(L2)_2$  molecules.

napththylethynyls  $[Zn(2F-L2)_2]$ , and a combination of both  $[Zn(3F-L2)_2]$ . A series of measurements reveal how fluorination influences crystal packing, controls self-assembly in films, and improves charge carrier mobility.

#### METHODS

The methods can be found in the Supporting Information.

#### RESULTS AND DISCUSSION

**Synthesis.** The synthesis of the fluorinated zinc complexes generally followed our previously published synthesis method for  $Zn(L2)_{2}$ ,<sup>42</sup> shown in Scheme 1. To install fluorine on the distal phenyls, we used 4-fluorobenzaldehyde instead of

benzaldehyde in the synthesis of the chalcone (step i in Scheme 1). To install fluorine on the pyrrolic 1-napthylethynyl groups, we simply used tributyl(4-fluoronaphthyl-1-ethynyl)stannane instead of tributyl(naphthyl-1-ethynyl)tin in the Stille coupling reaction iv. The ligands 1F-L2, 2F-L2, and 3F-L2 were purified by washing with methanol and were isolated as dark blue solids in high yields ( $\sim$ 90%). These ligands were less soluble in organic solvents, such as acetone and chloroform, than L2, with 3F-L2 having the lowest solubility. This could be due to hydrogen bonding with fluorine  $-C-F\cdots H$ . While  $Zn(L2)_2$  can be purified by solvent extraction, the fluorinated analogues required column chromatography purification to obtain pure products. The pure products were collected from the first blue-colored fraction in moderate yields of  $\sim$ 65%, lower than the yield of  $Zn(L2)_2$  (86%) due to loss during column purification. Note that incorporation of fluorine atoms on ADP increases polarity of the molecules, and this was evidenced by lower Rf values for the fluorinated complexes [0.65, 052, 0.51, and 0.46 for Zn((0- $(3F)-L2)_2$ , respectively] in thin layer chromatography (TLC) using the 1:1 DCM/hexane mobile phase. The identity and purity of all complexes were confirmed by <sup>1</sup>H NMR, MALDI-TOF MS, and elemental analysis.

The synthesis complexity (SC) for the new fluorinated complexes was calculated according to the method introduced by Po and co-workers and reported in Table S1.<sup>63</sup> The SC was 25.5, 23.5, and 25.6% for  $Zn(1F-L2)_2$ ,  $Zn(2F-L2)_2$ , and  $Zn(3F-L2)_2$ , respectively. These values are slightly larger than that of  $Zn(L2)_2$  (22.1%) due to lower yields and additional column chromatography step.<sup>42</sup> Nevertheless, these SCs are still very low compared to other NFAs.<sup>15</sup>

**Optical and Electrochemical Properties.** The UV–Vis absorption spectra in both chloroform and film are shown in Figure 3 and summarized in Table 1. The spectrum of  $Zn(L2)_2$  is included for comparison. The  $\lambda_{max}$  (nm), maximum molar absorptivity, and  $\lambda_{onset}$  (nm) of  $Zn((1F-3F)-L2)_2$  were all similar to those of  $Zn(L2)_2$  at around 700 nm, 140 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>, and 775 nm, respectively. Films were prepared by spin coating from 10 mg/mL solutions in chloroform. All films were dark blue, similar to the appearance of the  $Zn(L2)_2$  film. The film absorption spectra of all fluorinated complexes are similar, though the  $\lambda_{max}$  is slightly blue-shifted by ~4 nm from that of  $Zn(L2)_2$ . The  $\lambda_{onset}$  for all complexes is ~800 nm, corresponding to an optical gap of 1.55 eV. We conclude that fluorine substitution does not affect the absorption spectra significantly, as was previously observed for fluorinated  $Zn(WS3)_2$ .<sup>64</sup>

The cyclic voltammograms of the zinc(II) complexes in dichloromethane are shown in Figure 4, and the electrochemical properties are summarized in Table 2. The cyclic voltammetry (CV) patterns of the new complexes are similar to that of  $Zn(WS3)_2$ , with two reversible oxidation and two reversible reduction peaks. Figure 5 depicts the estimated HOMO and LUMO energy levels obtained from the onset of the first oxidation and first reduction peaks, respectively. Fluorination has minor effects on the estimated HOMO and LUMO energy levels, as previously observed for fluorinated  $Zn(WS3)_2$  complexes.<sup>64</sup> The largest change was observed for  $Zn(3F-L2)_2$ , where the HOMO decreased by 0.09 eV, whereas the LUMO only decreased by 0.02 eV relative to  $Zn(L2)_2$ , resulting in a larger energy gap of 1.64 eV.

**Thermal Properties.** To determine thermal stability, we performed thermogravimetric analysis (TGA), shown in Figure 6A. The decomposition temperatures of the complexes at 5% weight loss,  $T_{d5\%}$ , were all slightly above 400 °C [403, 405, and

#### Scheme 1. Synthesis Scheme for Zinc(II) Complexes<sup>a</sup>



"(i) MeOH, 5 M NaOH, 25 °C, 24 h (ii) MeNO<sub>2</sub>, DEA, MeOH, reflux, 24 h; ammonium acetate, 1-butanol, reflux, 24 h, (iii) NIS, CHCl<sub>3</sub>, acetic acid, 25 °C, 12 h in dark, (iv) Pd(PPh<sub>3</sub>)<sub>4</sub>, xylenes, 125 °C, 6 h, and (v) THF, NaH, 55 °C, 4 h, followed by CH<sub>2</sub>Cl<sub>2</sub>, ZnCl<sub>2</sub>/MeOH, 25 °C, 24 h.



Figure 3. UV-vis absorption spectra of zinc(II) complexes in (A) chloroform and in (B) films.

#### Table 1. Summary of Optical Properties of Zinc(II) Complexes in Solution and Film

	solution	film			
compound	$ \begin{array}{c} \lambda_{\max} \ (nm) \\ (\varepsilon, \times \ 10^3 \ M^{-1} \ cm^{-1}) \end{array} $	$\lambda_{\text{onset}}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{ m onset}$ (nm)	optical gap (eV)
$Zn(L2)_2$	330 (86), 373 (65), 664 (123), 700 (143)	775	727	805	1.54
$Zn(1F-L2)_2$	329 (85), 368 (66), 660 (123), 701 (141)	775	723	804	1.54
$Zn(2F-L2)_2$	329 (85), 367 (65), 661 (121), 700 (141)	775	723	799	1.55
$Zn(3F-L2)_2$	329 (83), 367 (65), 661 (120), 701 (139)	774	723	801	1.55

404 °C for  $Zn(1F-L2)_2$ ,  $Zn(2F-L2)_2$ , and  $Zn(3F-L2)_2$ , respectively] and a bit lower than that of  $Zn(L2)_2$  (415 °C). These decomposition temperatures are sufficiently high for most device applications. Differential scanning calorimetry (DSC)

was conducted for the complexes crystallized by vapor diffusion using THF as the solvent and pentanes as the antisolvent. All samples were heated to about 350 °C, well below the complex decomposition temperature, followed by cooling, see Figure 6B and Table S2. All samples show two or three endothermic peaks during the first heating cycle and no peaks during the cooling cycle. The second thermal cycles were also featureless (Supporting Information, Figure S18). These results are consistent with crystalline phases melting to an isotropic liquid upon heating, followed by glass formation upon cooling. The largest endothermic peak is the melting peak, with a melting temperature of 247, 227, and 247 °C for Zn(1F-L2)<sub>2</sub>, Zn(2F- $L2)_{2}^{2}$ , and  $Zn(3F-L2)_{2}$ , respectively. In comparison, the melting point for  $Zn(L2)_2$  is 229 °C.<sup>42</sup> The enthalpy of fusion ( $\Delta H_{fusion}$ ) is estimated at 7.6, 13, and 16 J/g for  $Zn(1F-L2)_2$ ,  $Zn(2F-L2)_2$ , and  $Zn(3F-L2)_2$ , respectively, compared to 44 J/g for  $Zn(L2)_2$ . The magnitude of  $\Delta H_{\text{fusion}}$  may be related to the magnitude of



**Figure 4.** Cyclic voltammograms of Zn complexes in 0.1 M TBAPF<sub>6</sub> dichloromethane solution with Fc/Fc<sup>+</sup> as an internal standard ( $E_{1/2}$  at 0.0 V).

intermolecular forces in the crystal, as well as how much of the sample is crystalline. The fluorinated complexes all showed a smaller endothermic peak at lower temperatures, 199, 177, and 157 °C for  $Zn(1F-L2)_2$ ,  $Zn(2F-L2)_2$ , and  $Zn(3F-L2)_2$ , respectively. These could be related to "melting" of the alkyl solubilizing groups.

Single-Crystal X-ray Diffraction. Crystal structures were obtained for Zn(2F-L2)<sub>2</sub> and Zn(3F-L2)<sub>2</sub>. Note that Zn(1F- $L2)_2$  could not grow large enough single crystals for the X-ray crystallography study. Figure 7A,D shows the ellipsoid plots for  $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$ , respectively. Both complexes have a distorted tetrahedral structure, typical for homoleptic Zn complexes of ADP. The fluoride groups are colored in green and are located at the expected positions on the complex. In both molecules, the dihedral angle between the two ligands was nearly identical, 59.2° (Figure 7B,E), and the intramolecular  $\pi - \pi$ stacking distances between proximal phenyls of one ligand and ADP-core pyrroles was in the 3.6–3.8 Å range (Figure 7C,F). The only chemical structural difference between the two molecules is the absence or presence of a fluorine on the distal phenyls, suggesting that fluorination at this position does not affect the geometry of the  $Zn^{2+}$  complexes.

By examining the complexes' crystal packing, we observe cofacial intermolecular  $\pi - \pi$  stacking interactions, depicted in Figure 7C,F. Zn(2F-L2)<sub>2</sub> has a cofacial parallel-displaced (PD)  $\pi - \pi$  stacking between the naphthyl group of one molecule and the ethynyl group of the neighboring molecule with distances of 3.4–3.7 Å and between the neighboring naphthyl groups with distances of 3.9–4.2 Å. In both cases, the polar C–F bonds are pointing in the opposite directions to minimize the net local dipole moment.<sup>61</sup> The C–F bonds appear to guide the cofacial  $\pi - \pi$  stacking of the conjugated system. Zn(3F-L2)<sub>2</sub> has a nearly



**Figure 5.** Estimated HOMO and LUMO energy levels were obtained by CV from the  $E_{\text{onset}}$  values in dichloromethane, using a value of -4.8 eV for Fc/Fc<sup>+</sup>. The energy levels for P3HT were estimated using the oxidation onset in films and the optical gap.

identical crystal packing as  $Zn(2F-L2)_2$ , pointing to the fluorinated naphthyl groups as a driver for self-assembly.

Figure S19 shows a subset image of crystal packing of  $Zn(2F-L2)_2$  with the *b*-axis out-of-plane. This image shows that the cofacial PD  $\pi-\pi$  stacking enables charge transport in 2 dimensions in the a-c plane. Figure S20 shows a subset image of crystal packing of  $Zn(2F-L2)_2$  with the *a* axis out-of-plane. In this illustration, two molecules (colored red and blue) are very close to each other with no clear dominant  $\pi-\pi$  stacking (also see Figure S21), while each appears to have close interaction between the distal phenyl on the central molecule with the naphthyl of the neighboring molecule (T-shaped). These interactions are expected to contribute to charge transport in the *b* axis.

To confirm that charge transport occurs in 3D, we calculated overlap integrals for pairs of adjacent complexes within the crystal unit cell. Table 3 reports the |Ve<sup>-</sup>| and |Vh<sup>+</sup>| for adjacent pairs that are close enough to give non-zero overlap integrals. Pair 1 corresponds to two neighboring molecules that have clear naphthyl-naphthyl cofacial PD stacking, and pair 2 corresponds to two neighboring molecules with naphthyl-ethynyl cofacial PD stacking. Both show non-zero overlap integrals, supporting 2-D charge transport in the a-c plane. Pair 3 corresponds to two molecules, where the closest interaction appears to be the Tshape orientation between a naphthyl or one molecule and a distal phenyl of the adjacent molecule (see Figure S20). Pair 4 corresponds to two close molecules, where we cannot tell which type of interaction dominates (none have cofacial orientation). The non-zero overlaps clearly show that charge transport can occur in these two pairs, confirming charge transport in the baxis. Interestingly, the overlap integrals are generally much larger for  $Zn(3F-L2)_2$  than for  $Zn(2F-L2)_2$ , despite having a nearly identical crystal structure. This suggests that the distal phenyl fluorination increases overlap integrals of both holes and electrons. The highest overlap integrals were obtained for the

Table 2. Electrochemical Properties of Zinc(II) Complexes in Dichloromethane<sup>a</sup>

compound	$E_{1/2}$ ox. (V)	$E_{\rm pa}$ (V)	$E_{1/2}$ red. (V)	$E_{\rm pc}$ (V)	$E_{\text{onsett}}$ ox (V)	$E_{\text{onsett}}$ red (V)	HOMO/LUMO (eV)	$E_{\rm gap}~({\rm eV})$
$Zn(L2)_2$	0.44, 0.71	0.47, 0.74	-1.26, -1.48	-1.30, -1.51	0.39	-1.18	-5.19/-3.62	1.57
$Zn(1F-L2)_2$	0.49, 0.73	0.52, 0.77	-1.25, -1.45	-1.29, -1.48	0.43	-1.15	-5.23/-3.65	1.58
$Zn(2F-L2)_2$	0.46, 0.72	0.51, 0.77	-1.29, -1.51	-1.35, -1.57	0.40	-1.20	-5.20/-3.60	1.60
$Zn(3F-L2)_2$	0.54, 0.78	0.60, 0.85	-1.25, -1.47	-1.32, -1.55	0.48	-1.16	-5.28/-3.64	1.64

"Note: Estimated HOMO (-IP) and LUMO (-EA) energy levels obtained by CV from the oxidation and reduction onsets in dichloromethane solution, using the value of -4.8 eV for Fc/Fc<sup>+</sup> vs vacuum.



**Figure 6.** (A) TGA plot of compounds showing 5% weight loss  $(T_{d5\%})$ ; (B) DSC plot of compounds on the first heating/cooling cycle.

naphthyl–ethynyl interaction, where  $|Vh^+|$  and  $|Ve^-|$  are 6.28 and 3.80 meV, respectively. The combination of both fluorination sites thus leads to significantly larger overlap integrals. The next highest level of overlap integrals is for the  $Zn(3F-L2)_2$  pair 4, where  $|Vh^+|$  and  $|Ve^-|$  are 1.80 and 2.84 meV, respectively. These values are similar to the highest values reported for  $Zn(L2)_2$  (1.3 and 3.0 meV for the  $|Vh^+|$  and  $|Ve^-|$ , respectively), which are also mainly due to T-shaped interactions (no cofacial orientation). These results highlight the potential advantage of encouraging cofacial  $\pi-\pi$  stacking to increase charge transport in these non-planar complexes.

**Photovoltaic Properties.** The fluorinated zinc complexes were tested with P3HT as the p-type material. The devices were fabricated using the inverted configuration ITO/ZnO/P3HT:NFA/MoO<sub>3</sub>/Ag. The active layer was spin-coated from a P3HT:Zn((1-3)F-L2)<sub>2</sub> solution in *o*-dichlorobenzene with a 1:1 weight ratio and a 20 mg/mL total concentration. Because all the films were spin-coated under the same conditions, they all had similar film thicknesses (80–100 nm). The films were annealed on a hot plate in a glove box for 15 min at 120 °C. The device data is summarized in Table 4 and the *I*–*V* curves for the best devices are compared in Figure 8. The best PCE was 5.4, 5.2, and 5.8% for Zn((1-3F)-L2)<sub>2</sub>, respectively. We were, therefore, able to improve the PCE of Zn(L2)<sub>2</sub> (5.5%) with fluorination at both positions.<sup>42</sup> For comparison, we obtained a

PCE of 4.3% for P3HT/PC<sub>61</sub>BM cells (similar conditions but using a 40 mg/mL total concentration). The P3HT:NFA cells all have larger  $V_{\rm OC}$  than the P3HT/PC<sub>61</sub>BM cells, consistent with the higher LUMO energy levels of the Zn complexes. The  $J_{\rm SC}$  values for the P3HT:Zn((1F-3F)-L2)<sub>2</sub> cells were similar or a bit higher than that of  $P3HT/PC_{61}BM$ . Because the Zn complex absorption spectra better complement that of P3HT than  $PC_{61}BM$ , one would expect much larger  $J_{SC}$  with the Zn complexes. The lower than expected  $J_{SC}$  values are due to the thinner film thickness of P3HT:Zn complex cells (80-100 nm) than the P3HT/PC<sub>61</sub>BM cells ( $\sim$ 200 nm), as was the case in our previous publications.<sup>41</sup> However, increasing the thickness of P3HT:Zn((1F-3F)-L2), films does not improve PCE, indicating non-optical issues limiting these fullerene-free devices. Note that because all the P3HT: $Zn((1F-3F)-L2)_2$  films had similar thicknesses and all the Zn complexes have the same absorption spectra and molar absorption coefficients, the differences in PCE observed between the P3HT:Zn complexes devices are most likely not caused by differences in absorption.

To further understand the PCE difference between the electron acceptors, we investigated the role of charge carrier recombination. Figure 9A shows  $J_{SC}$  as a function of light intensity on a double-logarithmic scale. The extracted power law exponents for  $Zn((1F-3F)-L2)_2$  are reported in Table 4. All power law exponents were close to unity, indicating negligible bimolecular recombination in these thin solar cells. Figure 9B shows the  $V_{\rm OC}$  as a function of light intensity on a semilogarithmic scale. Fullerene PC<sub>61</sub>BM was used as a reference because it is considered a trap-free material. The carrier traps in the P3HT/PC<sub>61</sub>BM cell are, therefore, assumed to be mostly from P3HT.<sup>65</sup> The data were fitted into a linear function and the slopes of the functions were extracted in terms of multiples of kT/q. A kT/q slope greater than one indicates the presence of trap-assisted recombination.<sup>66-69</sup> The results are summarized in Table 4. The slope of P3HT/PCBM cells is 1.33 kT/q and is close to the reported 1.25 kT/q.<sup>67,70</sup> The slope values for P3HT: $Zn((1F-3F)-L2)_2$  devices are 1.4 kT/q, 1.6 kT/qq, and 1.6 kT/q, respectively. These are all higher than those previously reported for P3HT: $Zn(L2)_2$ , at 1.3 kT/q.<sup>42</sup> For the fluorinated complexes,  $Zn(1F-L2)_2$  shows the least trap-assisted recombination, consistent with having the highest  $J_{SC}$ , while the other two fluorinated materials have higher but similar levels of trap-assisted recombination, suggesting that F on the naphthyl increases trap-assisted recombination.

Charge Transport Properties. The complexes' charge transport properties were investigated using the space-chargelimited-current (SCLC) method in both neat films and blends with P3HT (annealed using the same conditions as OPV devices). The hole mobility measurement was tested by using the ITO/PEDTO:PSS/zinc complex/MoO<sub>3</sub>/Ag device structure, and the electron mobility measurement was tested using the ITO/ZnO/zinc complex/Ca/Al device structure. The SCLC graphs are shown in the Supporting Information section, and the results are summarized in Table 5. The hole mobilities of the fluorinated materials are high, from  $0.8 \times 10^{-3}$  to  $1.0 \times 10^{-3}$  $cm^2 V^{-1} s^{-1}$ , 1 order of magnitude higher than that of  $Zn(L2)_2$ , at  $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Fluorination is, therefore, beneficial for hole mobility in these complexes. The hole mobility of  $Zn(1F-L2)_2$  with fluorine on the distal phenyls is slightly lower than that of the other two complexes, which both have fluorine on the naphthyl groups. The electron mobility values of Zn(1F-L2)<sub>2</sub> and Zn(L2)<sub>2</sub> are similar, at  $2.4 \times 10^{-5}$  and  $4.2 \times 10^{-5}$  cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, respectively, while the complexes with fluorine on the



**Figure 7.**  $Zn(2F-L2)_2$ : (A) ellipsoid plots at 50% probability, (B) dihedral angle between the two ligands, and (C) intermolecular (in black) and intramolecular (in red)  $\pi - \pi$  stacking distances.  $Zn(3F-L2)_2$ : (D) ellipsoid plots at 50% probability, (E) dihedral angle between the two ligands, and (F) intermolecular (in black) and intramolecular (in red)  $\pi - \pi$  stacking distances.

# Table 3. Summary of $|Ve^-|$ and $|Vh^+|$ from Charge Transfer Integrals<sup>*a*</sup>

pair	identified $\pi - \pi$ stacking interaction	Vh <sup>+</sup>  ,  Ve <sup>-</sup>   (meV) Zn(2F-L2) <sub>2</sub>	Vh <sup>+</sup>  ,  Ve <sup>-</sup>   (meV) Zn(3F-L2) <sub>2</sub>
1	naphthyl-naphthyl (PD)	0.03, 0.99	0.11, 0.60
2	napthyl—ethynyl (PD)	0.94, 1.11	6.28, 3.80
3	distal phenyl–napththyl (T)	0.72, 0.30	0.59, 1.95
4	several (T)	0.21, 1.15	1.80, 2.84
<sup>a</sup> The	red molecule served as t	the reference molecu	ile for all adjacent

The red molecule served as the reference molecule for all adjacent pairs.

naphthyl groups  $(Zn(2F-L2)_2 \text{ and } Zn(3F-L2)_2)$  have much higher electron mobility, at ~2.0 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. These results indicate that fluorination of the naphthyl groups is beneficial for electron mobility. In blends with P3HT, the hole mobility was unusually high for P3HT-based OPVs, ranging from 1.6 × 10<sup>-3</sup> to 3.4 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This raises the possibility that the zinc complexes contribute to hole transport in blends. Electron mobility was relatively low for Zn(1F-L2)<sub>2</sub> and Zn(2F-L2)<sub>2</sub>, about 1 magnitude lower than those of the neat film, suggesting a non-ideal blend morphology. Zn(3F-L2)<sub>2</sub> showed similar electron mobility to that in neat films, suggesting good percolation pathways for electron transport in P3HT:Zn-(3F-L2)<sub>2</sub> blends.

Grazing-Incident Wide-Angle X-ray Diffraction Study. To better understand the effect of fluorination on charge



Figure 8. Current density—voltage characteristics of solar cells with an effective area of 0.2  $\text{cm}^2$  by using simulated AM1.5 G illumination at 100 mW cm<sup>-2</sup>.

transport and photovoltaic properties, we investigated the morphology of neat and blended film using the grazing-incident wide-angle X-ray diffraction (GIWAXD) technique. The 2D GIWAXD patterns of the spin-coated neat films, together with the corresponding intensities along the horizontal and vertical directions versus the scattering vector (q) plots, are shown in Figure 10. Peaks that match the calculated powder diffraction

Table 4. Organic Photovoltaic Device Characteristics for Blends with P3HT as the p-Type Material<sup>a</sup>

n-type material	$J_{\rm SC}~({\rm mA~cm^{-2}})$	$V_{\rm OC}$ (V)	FF	PCE (%)	power law exponent	$V_{\rm OC}$ slope (times of $kT/q$ )
$Zn(1F-L2)_2$	14.2 $(13.7 \pm 0.7)$	$0.72~(0.72\pm0.02)$	$0.53 \ (0.52 \pm 0.01)$	$5.4(5.2 \pm 0.2)$	1.05	1.44
$Zn(2F-L2)_2$	$11.7 (11.4 \pm 0.2)$	$0.79~(0.77\pm0.02)$	$0.56~(0.56\pm0.01)$	$5.2 (4.9 \pm 0.2)$	1.04	1.62
$Zn(3F-L2)_2$	$13.2 (13.0 \pm 0.6)$	$0.71~(0.70\pm0.01)$	$0.62 \ (0.61 \pm 0.01)$	$5.8(5.6 \pm 0.2)$	1.05	1.63
PC <sub>60</sub> BM	$12.6 (12.1 \pm 0.4)$	$0.59~(0.59\pm0.00)$	$0.58~(0.58\pm0.02)$	$4.3 (4.1 \pm 0.1)$	1.04	1.33

"Note: Averages were calculated for at least five devices. k is Boltzmann's constant, T is the temperature, and q is the elementary charge.



**Figure 9.** A)  $J_{SC}$  as a function of light intensity on a double-logarithmic scale; (B)  $V_{OC}$  as a function of light intensity on a semilogarithmic scale.

patterns were assigned with the (hkl) Miller indices. All the samples, except for Zn(3F-L2)<sub>2</sub>, show an obvious amorphous content, which could be attributed to the slow kinetics to crystallize. Poor crystal orientation is observed for Zn(L2)<sub>2</sub> with sharp (010) and (101) reflections and the  $\pi-\pi$  stacking peak with a distance of 4.5 Å. The (010) reflection is more concentrated on the vertical direction, suggesting that a significant number of crystals orients with their *b*-axis (a triclinic unit cell)<sup>42</sup> in the out-of-plane direction.

 $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$  exhibit similar uniaxial GI-WAXD patterns, except that  $Zn(3F-L2)_2$  has a much higher crystallinity. Given both (040) reflections appear in the vertical direction with a good match to the calculated patterns in Figure S31, it is inferred that these patterns are *b*-uniaxial patterns. For these two complexes, most of the crystals thus orient with their *b*-axes out-of-plane, where the alkyl groups are interacting with the substrate. The  $\pi$ - $\pi$  stacking distances are ~4.2 Å for Zn(2F-L2)<sub>2</sub> and 3.7 Å for Zn(3F-L2)<sub>2</sub>. Because we could not grow large enough single crystals for Zn(1F-L2)<sub>2</sub>, its structure is not



**Figure 10.** GIWAXD diffraction patterns of (a)  $Zn(L2)_2$ , (b)  $Zn(1F-L2)_2$ , (c)  $Zn(2F-L2)_2$ , and (d)  $Zn(3F-L2)_2$ . Intensity vs *q* plot for inplane (red), out-of-plane (blue), and the corresponding powder diffraction pattern (black) for (e)  $Zn(L2)_2$ , (f)  $Zn(1F-L2)_2$ , (g)  $Zn(2F-L2)_2$ , and (h)  $Zn(3F-L2)_2$ . Black dotted lines indicate sharp peaks and green dotted lines indicate  $\pi-\pi$  stacking.

determined. However, the indexing of the GIWAXD pattern in Figure S31 shows a similar crystal lattice with the same *b*-uniaxial orientation for  $Zn(1F-L2)_2$ . The  $\pi-\pi$  stacking is observed at a distance of 4.3 Å.

The crystallite dimensions (grain sizes) were estimated using the Scherrer equation and are reported in Table 6.<sup>71,72</sup> The unfluorinated  $Zn(L2)_2$  film has crystallite sizes in the out-ofplane and the in-plane directions of 22.6 and 14.4 nm, respectively. The complexes with -F on the distal phenyls,  $Zn(1F-L2)_2$ , and on the naphthyl position,  $Zn(2F-L2)_2$ , show smaller crystallites with out-of-plane and in-plane dimensions of ~13 and ~10.5 nm, respectively. The complex with -F at both positions,  $Zn(3F-L2)_2$ , has crystallites with estimated sizes between 15 and 16 nm in both directions. Fluorination of both positions thus results in larger grain sizes than fluorination at

Table 5. Charge Carrier Mobility of Zinc(II) Complexes in Neat and Blend Films Determined Using the SCLC Method

	neat $\mu_{\rm h} ~({\rm cm}^2~{ m V}^{-1}~{ m s}^{-1})$	neat $\mu_{\rm e}  ({\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1})$	blend $\mu_{\rm h}  ({\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1})$	blend $\mu_{\rm e} ~({\rm cm}^2 ~{ m V}^{-1} ~{ m s}^{-1})$
$Zn(1F-L2)_2$	$(8.1 \pm 1.5) \times 10^{-4}$	$(2.4 \pm 0.2) \times 10^{-5}$	$(1.6 \pm 0.6) \times 10^{-3}$	$(1.7 \pm 0.4) \times 10^{-5}$
$Zn(2F-L2)_2$	$(1.0 \pm 0.4) \times 10^{-3}$	$(2.0 \pm 2.1) \times 10^{-4}$	$(3.4 \pm 1.8) \times 10^{-3}$	$(1.5 \pm 0.2) \times 10^{-5}$
$Zn(3F-L2)_2$	$(9.8 \pm 3.8) \times 10^{-4}$	$(1.9 \pm 1.5) \times 10^{-4}$	$(1.9 \pm 1.0) \times 10^{-3}$	$(2.2 \pm 0.5) \times 10^{-4}$
$Zn(L2)_2$	$1.0 \times 10^{-4a}$	$4.2 \times 10^{-5a}$	$3.1 \times 10^{-4a}$	$2.4 \times 10^{-5a}$

<sup>*a*</sup>Published data.<sup>42</sup>

Table 6. Summary of Crystallite Measurements of Neat Films of the Complexes and P3HT:Complex Blend Films

	size of complex	in neat film	P3HT properties in blends with complex		
compound	out-of-plane (nm)	in-plane (nm)	size (nm)	lamellar spacing (nm)	
$Zn(L2)_2$	22.6	14.4	10.9	1.85	
$Zn(1F-L2)_2$	12.8	10.4	8.67	1.83	
$Zn(2F-L2)_2$	13.3	10.5	12.3	1.85	
$Zn(3F-L2)_2$	16.3	15.2	10.9	1.82	

only one of the positions, though they were not quite as large as those of  $Zn(L2)_2$ .

The GIWAXS diffraction patterns for blends with P3HT are shown in Figure 11. In all the films, we observe the characteristic



**Figure 11.** GIWAXD diffraction patterns for P3HT blends with (a)  $Zn(L2)_2$ , (b)  $Zn(1F-L2)_2$ , (c)  $Zn(2F-L2)_2$ , and (d)  $Zn(3F-L2)_2$ . Intensity versus *q* plots for in-plane (red), out-of-plane (blue), and the corresponding powder diffraction patterns (black) for (e)  $Zn(L2)_2$ , (f)  $Zn(1F-L2)_2$ , (g)  $Zn(2F-L2)_2$ , and (h)  $Zn(3F-L2)_2$ .

P3HT diffraction peaks with lamellar reflections in the out-ofplane direction and  $\pi$ – $\pi$  stacking diffraction peak in the in-plane direction, pointing to mainly edge-on orientation. In all blends, the P3HT lamellar spacing was 1.8 nm, which was slightly larger than that of neat P3HT films (1.68 nm) and larger than those in P3HT/PC<sub>61</sub>BM (1.71 nm) and P3HT/PC<sub>71</sub>BM (1.74 nm) blends.<sup>73</sup> This indicates a lower degree of P3HT crystallinity in blends. A similar trend is observed in NFA molecules: the angular width of (040) peaks in the blends is higher than that in the neat films, suggesting more disorientation of the zinc complex in the blends. The diffraction patterns for P3HT:Zn-(L2)<sub>2</sub> blends are dominated by the P3HT diffraction peaks, with a weak indication of the complex crystallizing in the film, similar to our previous publication.<sup>42</sup> The P3HT:Zn(1F-L2)<sub>2</sub> film shows certain peaks that correspond to Zn(1F-L2)<sub>2</sub>. Judging by the uniaxial pattern, Zn(1F-L2)<sub>2</sub> crystals keep the same orientation as in the neat film. Similarly, P3HT:Zn(2F-L2)<sub>2</sub> and P3HT:Zn(3F-L2)<sub>2</sub> films also exhibit *b*-uniaxial patterns with the *b*-axis out-of-plane. These results strongly suggest that fluorination can increase the tendency of the zinc complexes to crystallize in the blend films.

In the blend films, the P3HT crystallite sizes (Table 6) were estimated using the (100) reflection. The P3HT crystallite sizes were ~11, ~9, ~12, and ~11 nm in blends with  $Zn(L2)_2$ ,  $Zn(1F-L2)_2$ ,  $Zn(2F-L2)_2$ , and  $Zn(3F-L2)_2$ , respectively. Fluorination on the distal phenyls results in slightly smaller P3HT crystallites, while pyrrolic naphthyl groups results in slightly larger crystallites. A combination of both, as seen with  $Zn(3F-L2)_2$ , results in P3HT crystallite sizes similar to that in blends with  $Zn(L2)_2$ . While the crystallite size of P3HT varies a little bit depending on the Zn complex that it is mixed with, the size is on the nanoscale in all blends, which is favorable for OPV devices. We conclude that fluorination has only a minor effect on P3HT self-assembly in blends and surmise that any improvements in OPV performance would be the result of changes in the complex phase.

The relative crystallinity in neat and blend films was estimated by separating the crystalline peaks from the amorphous halos, see Figure S32 and Table S4. In neat films,  $Zn(3F-L2)_2$  and  $Zn(1F-L2)_2$  have the highest % crystallinity (38 and 37%, respectively), while  $Zn(2F-L2)_2$  has the lowest (10%). These results do not correlate with charge carrier mobility data. The estimated relative crystallinity was similar (60–65%) in all blends, probably because P3HT dominates. We therefore cannot conclude the influence of the degree of crystallinity on charge carrier mobilities for zinc complexes in blend films.

Atomic Force Microscopy. The surface of the OPV active layers was imaged using an atomic force microscope. The 1  $\mu$ m  $\times$  1  $\mu$ m phase and height images are shown in Figure 12, and the 5  $\mu$ m × 5  $\mu$ m images are given in the Supporting Information section. The height images show that the films are smooth, with surface roughness values of 4.4 nm for P3HT:Zn(1F-L2)<sub>2</sub>, 9.6 nm for P3HT:Zn(2F-L2)<sub>2</sub>, and 7.8 nm for P3HT:Zn(3F-L2)<sub>2</sub> films. The phase images show more defined features, with lighter and darker parts related to domains having different adhesion and/or mechanical properties.<sup>70</sup> In the 1  $\mu$ m × 1  $\mu$ m phase images, the *n*-type and *p*-type materials appear to be phase separated with irregular shaped domains, whose size ranges 15-35 nm for P3HT:Zn(1F-L2)<sub>2</sub>, 30-50 nm for P3HT:Zn(2F-L2)<sub>2</sub>, and 20–40 nm for P3HT:Zn(3F-L2)<sub>2</sub> blends. To further characterize the surface composition of the blends, we analyzed the surface of neat and blend films by X-ray photoelectron spectroscopy (XPS) (see Figure S33). Generally, the presence of sulfur (from P3HT) was detected in all films. In addition, the XPS spectra of neat NFA films show clear peaks assigned to fluorine and zinc elements. However, those peaks are much smaller or not present in the blend films, suggesting that the surface is composed mainly of P3HT. It is not clear why we did not observe the typical P3HT nanofibrils in these surface images, despite the usual diffraction patterns by GIWAXD. Further experiments are needed to understand this observation.



**Figure 12.** AFM (A–C) phase and (D–F) height images for the optimized OPV films of P3HT:Zn(II) complex blends. All films were annealed at 120 °C for 15 min, and all images are 1  $\mu$ m × 1  $\mu$ m. In each phase image, a typical domain is circled with the corresponding size labeled. Rq is the surface roughness.

## CONCLUSIONS

A series of fluorinated Zn complexes were synthesized and characterized. The effects of fluorination at the para position of the distal phenyls and at the 4th position of the naphthyl group on photovoltaic properties were compared. All three new complexes had relatively low synthetic complexities, in the range of 23.5-25.6%. Fluorination did not affect the optical properties of  $Zn(L2)_2$  and had minor effects on the electrochemical properties. All complexes are thermally stable with 5% decomposition temperatures >400 °C. The crystal packing of  $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$  revealed clear cofacial PD  $\pi-\pi$ stacking involving the fluorinated naphthylethynyl groups, enabling charge transport in two dimensions (a-c plane). Other  $\pi - \pi$  stacking orientations (like T-shaped) enable charge transport in the other dimension (along the b axis). The three complexes were tested in OPVs using P3HT as the donor, and the best PCEs were 5.2, 5.4, and 5.8% for  $Zn(2F-L2)_2$ ,  $Zn(1F-L2)_2$  $L2)_{21}$  and  $Zn(3F-L2)_{21}$  respectively, compared to 5.5% for  $Zn(L2)_2$ . All devices had relatively low bimolecular charge carrier recombination. The fluorinated complexes have higher trap-assisted recombination than  $Zn(L2)_2$ . Fluorination was beneficial for hole transport, as hole mobility (by SCLC) in neat films increased from  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for Zn(L2)<sub>2</sub> to 0.8–  $1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the fluorinated complexes. On the other hand, only the complexes with fluorine on the naphthyl groups had improved electron mobility from  $4.2 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$  for Zn(L2)<sub>2</sub> and Zn(1F-L2)<sub>2</sub> to 2.0 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for  $Zn(2F-L2)_2$  and  $Zn(3F-L2)_2$ . This is consistent with the importance of having a cofacial  $\pi - \pi$  stacking orientation for electron transport. In blends, electron mobility was the highest for  $Zn(3F-L2)_2$ , with a mobility similar to the  $Zn(3F-L2)_2$  neat film at  $\sim 2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, resulting in a more balanced charge transport in P3HT:Zn(3F-L2)<sub>2</sub> blends and consistent with the higher  $J_{SC}$ , FF, and PCE observed. Morphologies of neat

and blend films were examined by GIWAXD. In neat films, the fluorinated complexes showed a preferred crystal orientation with the *b*-axis out-of-plane. The diffraction patterns also show that the fluorinated complexes crystallized in the blends. In this study, we found that F on the naphthyl groups promotes a cofacial PD intermolecular  $\pi-\pi$  stacking orientation, which is associated with increased electron mobility. Although F increased the electron mobility of these complexes to a magnitude that is associated with very high PCE for other systems, the optimal film thickness is still limited to ~100 nm, limiting the overall PCE. More research is required to understand the limitations, so that we can take full advantage of these interesting hybrid organic/inorganic coordination compounds in organic electronic applications.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c09734.

Experimental section; synthetic complexity calculations; NMR and MALDI-TOF MS spectra of new compounds; DSC second heating and cooling cycles; crystal packing images; charge carrier mobility data; AFM images; crystallite size determination details; and crystal structure data (PDF)

Crystallographic information on Zn(2F-L2)<sub>2</sub> (CCDC = 2120093) (CIF)

Crystallographic information on  $Zn(3F-L2)_2$  (CCDC = 2120094) (CIF)

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#### Notes

The authors declare no competing financial interest.

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