Synthesis and Optoelectronic Properties of a Solution-processed Red-emitting Tetra(arylvinyl)anthracene Cruciform

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Abstract:

In this paper, we report the synthesis and optoelectronic properties of a new anthracene-centered cruciform, 2,6-bis(9,9-di(2-ethylhexyl)fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)anthracene (**FCA**). **FCA** was prepared by the Heck coupling 2,6-bis(diethoxylphosphorylmethyl)-9,10-dibromoanthracene and 9-(2-ethylhexyl)-3-vinylcabazole, followed by the Wittig-Horner reaction with 9,9-di(2-ethylhexyl)-2-formylfluorene. The existence of strongly twisted 9,10-branch made **FCA** exhibit moderate aggregation-enhanced emission and piezofluorochromism, and the introduction of numerous branched alkyl chains render **FCA** with good solubility and film-forming ability. **FCA** could be used

as solution-processed light-emitting layer to afford red emission with peak wavelength of 612 nm and maximal luminous efficacy of 1.3 cd/A.

Keywords: Center-crossed conjugated molecule; Anthracene-based cruciform; Piezofluorochromism; Solution-processed oligomer; Aggregation-enhanced emission; Solid-state red emitting material.

1.1 Introduction:

Conjugated organic molecules have attracted much attention due to their potential applications in organic optical and optoelectronic fields, and much effort has devoted to the design and synthesis of new luminogens with unique structures and optoelectronic properties. While the linear π -conjugated organic molecules have been the mainstay of optical and optoelectronic materials, recently, higher orders, especially two dimensional arylene-centered oligomers, have started to draw serious research interest, and some benzene-, thiophene-, anthracene-, pyrazine-, benzobisoxazole-, and benzobisthiophene-centered cruciforms have been designed, synthesized and their optical and optoelectronic properties investigated.[1–10] These new configuration materials with unique geometric and electronic structures have greatly widened the scope of molecular candidates applicable in chemosensors, molecular switches, nonlinear optical materials, field effect transistors, and photovoltaic and electroluminescence devices.[11–15]

We have been interested in 2,6,9,10-tetra(arylvinyl)anthracene derivatives due to their unique π -centered structure and distorted conformation. Compared to the

45 extensively investigated benzene-centered and other aryl-centered analogues,
46 2,6,9,10-tetra(arylvinyl)anthracene cruciforms have an asymmetric π -center and a
47 strongly twisted 9,10-branch, which could render them with unique aggregation
48 behaviors and optical properties.[16–18] For example, donor- and/or acceptor-capped
49 cruciforms show large and enhanced two-photon absorption cross sections, and
50 pyridine- and/or dibutylaniline-capped cruciforms exhibit the selectively
51 fluorescence sensing on metal ions and piezofluorochromism based on 9,10-bis-
52 (arylvinyl)anthracene branch,[19–22] etc. Since center-crossed cruciforms have
53 multiple conjugation pathways for intramolecular charge transfer, donor- and/or
54 acceptor-substituted anthracene-centered cruciforms usually exhibit more
55 bathochromic shift emission than their linear building blocks 9,10- and 2,6-bis(aryl-
56 vinyl)anthracenes.[23–25] Moreover, the existence of twisted branch 9,10-bis(aryl-
57 vinyl)anthracene could alleviate from intermolecular tight stacking and strong
58 interactions, which should improve the solid-state fluorescence efficiency and could
59 be promising light-emitting materials with unique structure.[26–27] However, such
60 tetra(arylvinyl)anthracene cruciforms usually have large and rigid conjugation
61 skeleton, which is not beneficial to solubility and film fabrication by vacuum
62 deposition. In the current work, we have introduced several branched alkyl chains into
63 the molecular peripheries to improve the solubility and the film-forming capacity. We
64 now report the synthesis and optoelectronic properties of a new and
65 solution-processed 2,6,9,10-tetra(arylvinyl)anthracene cruciform, 2,6-bis(9,9-di(2-
66 ethylhexyl)fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)-

anthracene (**FCA**).

1.2 Experimental Section

1.2.1 Materials

Acetonitrile (MeCN) and tetrahydrofuran (THF) (over metallic sodium) and triethylamine (over CaH₂) were distilled before use. Carbazole, 2-bromofluorene and other solvents and reagents (analytical grade) were commercial available and used as received, unless otherwise claimed. 2,6-Bis(diethylphosphorylmethyl)- 9,10-dibromo-anthracene was from the previous work.[28]

1.2.2 Preparation of aqueous dispersion and ground sample.

The stock solution of **FCA** in THF with a concentration of 1.0×10^{-4} M was prepared and reserved. THF/water mixtures with different water fractions (aqueous dispersion) were prepared by slowly adding distilled water into the THF solution of **FCA** under ultrasound at room temperature, and the final concentration was kept at 1.0×10^{-5} M. Ground sample was prepared by grinding **FCA** powder on a glass plate with a metal spatula at room temperature.

1.2.3 Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker-AC500 (500 MHz) spectrometer with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed on a Perkin-Elmer 2400. UV-vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Emission spectra were measured with a Hitachi F-4600 spectrophotometer. The peak

wavelength of the lowest energy absorption band was used as the excitation wavelength for the PL measurement. The fluorescence quantum yield (Φ) was determined at room temperature by the dilution method using rhodamine B in methanol as the reference. [29] Cyclic voltammetry (CV) was performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk (diameter = 3 mm) as the working electrode, a platinum wire as the auxiliary electrode with a porous ceramic wick, and Ag/Ag⁺ as the reference electrode standardized by the redox couple ferrocenium/ferrocene. All solutions were purged with a nitrogen stream for 10 min before measurement. The procedure was performed at room temperature, and a nitrogen atmosphere was maintained over the solution during measurements. [30-32] Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were performed under nitrogen atmosphere on Netzsch DSC 204F1 and Netzsch 209F1 analyzers at heating rates of 10 °C/min and 20 °C/min, respectively.

1.2.4 Device Fabrication

Indium-tin oxide (ITO) coated glass with a sheet resistance of 15–20 Ω/cm^2 was used as the cathode whose substrate was pre-patterned by photolithography to give an effective device size of 6.25 mm². Then, it was cleaned in an ultrasonic bath with acetone, detergent, deionized water, and isopropanol as the clean agent. After being dried in an oven, it is treated with oxygen plasma for 4 min, and then 40 nm of PEDOT:PSS layer was spin-coated and baked overnight in a vacuum oven at 80 °C. On the top of above active layer, a 60 nm of FCA bulk emitting layer was spin-casted

from its chloroform solution (12 mg/mL). The **FCA** solution in chloroform has been filtered through a 0.45 μm PTFE filter before spin coating. Then 1,3,5-tri(phenyl-2-benzimidazol-yl)benzene (TPBi) as electron-transporting layer (50 nm) were vacuum deposited. Finally, 0.5 nm of LiF film and 100 nm of Al film was vacuum deposited to form the anode. The base pressure for vacuum deposition was at of 3×10^{-4} Pa. The thickness of each deposition layer was monitored using a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). Electroluminescence (EL) spectra were measured by a PR650 fluorescence spectrophotometer. Luminance-voltage and current density-voltage characteristics were recorded simultaneously by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.

1.2.5 Synthesis

9,10-Bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)-2,6-bis(diethylphosphorylmethyl)-anthracene

A dried pressure tube was added 2,6-bis(diethylphosphorylmethyl)-9,10-dibromoanthracene (0.21 g, 0.33 mmol), 9-(2-ethylhexyl)-3-vinyl-carbazole (0.36 g, 1.18 mmol), $\text{Pd}(\text{OAc})_2$ (7.4 mg, 0.033 mmol), tri(*o*-toyl)phosphine (68 mg, 0.23 mmol), *N,N*-dimethylformamide (DMF) (1.5 mL), and triethylamine (1.5 mL), and then purged by nitrogen and sealed with a Teflon screw top. The mixture was refluxed for 24 h and then extracted with dichloromethane. The solvent was removed and the crude product was separated by column chromatography on silica gel using petroleum ether/ethyl acetate (1/1) as the eluent. Yield: 0.21 g (58%). ^1H NMR (500 MHz,

CDCl₃, ppm): δ 8.48 (d, 2H), 8.38 (s, 2H), 8.34 (s, 2H), 8.18 (d, 2H), 7.93 (d, 2H), 7.86 (d, 2H), 7.49 (m, 8H), 7.28 (d, 2H), 7.12 (d, 2H), 4.24 (m, 4H), 4.03 (m, 8H), 3.36 (d, 4H), 2.13 (m, 2H), 1.22 (m, 16H), 0.96 (t, 12H), 0.90 (t, 12H).

2,6-Bis(9,9-di(2-ethylhexyl)fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)anthracene (FCA)

Potassium *tert*-butoxide (0.16 g, 1.43 mmol) was added to a dried one-neck flask containing the solution of 9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)-2,6-bis-(diethylphosphorylmethyl)anthracene (0.17 g, 0.16 mmol) and 9,9-di(2-ethylhexyl)-2-formylfluorene (0.19 g, 0.45 mmol) in anhydrous THF (10 mL) under nitrogen. The mixture was stirred over night at room temperature and then 100 mL of methanol was added. The precipitate was collected and purified by a column chromatography on silica gel using petroleum ether/dichloromethane (2/1) as the eluent. Yield: 0.21 g (82%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.52 (d, 2H), 8.48 (s, 2H), 8.42 (s, 2H), 8.22 (d, 2H), 8.01 (d, 2H), 7.94 (d, 2H), 7.86 (d, 2H), 7.64 (t, 4H), 7.58 (t, 2H), 7.50 (m, 8H), 7.30 (m, 10H), 7.23 (m, 4H), 4.27 (d, 4H), 2.16 (t, 2H), 1.98 (m, 8H), 1.05 (m, 4H), 0.80 (m, 12H), 0.75 (m, 12H), 0.70 (t, 6H), 0.65 (m, 24H), 0.56 (t, 6H), 0.48 (t, 24H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 150.98, 150.67, 141.42, 141.11, 141.00, 140.91, 138.29, 135.82, 135.77, 135.71, 134.20, 133.03, 130.28, 129.64, 129.58, 128.57, 128.12, 127.29, 126.69, 126.36, 126.10, 125.92, 124.47, 124.01, 123.29, 122.85, 122.19, 121.71, 120.51, 119.71, 119.55, 119.12, 118.78, 109.31, 109.22, 54.75, 47.56, 44.61, 39.49, 34.51, 33.56, 31.93, 29.71, 28.88, 27.00, 26.85, 24.42, 23.11, 22.68, 14.80, 14.00, 10.34.

9-(2-ethylhexyl)-3-formylcarbazole

To a cooled flask in an ice bath was added phosphoryl chloride (0.6 mL, 5.9 mmol) and anhydrous DMF (1.4 mL, 17.7 mmol) under nitrogen. To this mixture was added 9-(2-ethylhexyl)carbazole (1.5 g, 5.4 mmol, in 20 mL sym-dichloroethane). After stirring for 1 h, the reaction temperature was raised to 90 °C and left for 8 h. The mixture was cooled and poured into ice water and extracted with dichloromethane. The solvent was evaporated and the crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1/10) as the eluent. Yield: 1.3 g (78.3%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 10.08 (s, 1H), 8.60 (s, 1H), 8.15 (d, 1H), 8.01 (d, 1H), 7.54 (t, 1H), 7.47 (t, 2H), 7.33 (t, 1H), 4.35 (d, 2H), 1.95 (m, 1H), 1.50 (m, 4H), 1.23 (m, 4H), 0.95 (t, 6H).

9,9-Di(2-ethylhexyl)-2-formylfluorene

To a solution of 2-bromo-9,9-di(2-ethylhexyl)-fluorene (3.5 g, 6.03 mmol) in anhydrous THF (15 mL) was added dropwise *n*-BuLi (2.5 mL, 7.24 mmol) at -78 °C. After stirring for 1 h, anhydrous DMF (2.87 g, 35.0 mmol) was added and stirred for an additional 12 h at 0 °C. The resulting mixture was added to water and extracted with dichloromethane. The organic layer was separated and washed with diluted HCl and then saturated aqueous NaHCO₃. The solvent was removed by evaporation and the residue was purified by column chromatography using dichloromethane/petroleum ether (1/10) as the eluent to give a colorless oil. Yield: 1.43 g (45%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 10.05 (s, 1H), 7.85 (d, 1H), 7.80 (t, 1H), 7.77 (t, 1H), 7.70 (d, 1H), 7.67 (s, 1H), 7.61 (d, 1H), 7.55 (d, 1H), 1.98 (d, 4H), 1.50 (m, 2H), 1.23 (m,

16H), 0.95 (t, 12H).

Scheme 1. The structure and synthetic route of anthracene-centered cruciform (**FCA**) studied in this paper.

1.3 Results and discussion

1.3.1 Synthesis and characterization

Carbazole- and/or fluorene-capped 2,6,9,10-tetravinylanthracene derivatives have the large and rigid conjugation skeleton, which leads to the poor solubility in common organic solvents. Here we have introduced numerous branched alkyl chains (2-ethyl-hexyl) to the skeleton periphery in order to obtain highly soluble anthracene-based cruciform. Indeed, **FCA** is soluble in many common organic solvents, such as dichloromethane, chloroform, THF, acetonitrile, toluene, and chlorobenzene, etc. The

resulting solutions with 10 mg/mL could smoothly pass through 0.45 μm PTFE filter. We choose the Heck coupling as the first step reaction, which produces the highly soluble and decreased polar intermediate containing 2,6-bis(diethylphosphinemethyl) moieties. After Wittig-Horner reaction, this polar intermediate is changed into weakly polar **FCA**. The differential polarities among them make the separation easy. The structure and composition of target cruciform **FCA** was unambiguously confirmed by NMR and elemental analysis.

1.3.2 Emission spectra of solution and aqueous dispersion

Fig. 1 shows the absorption and emission spectra of **FCA** in THF solution. There are two absorption bands whose peak wavelengths are at 385 and 459 nm, respectively. The higher energy band is ascribed to arylvinyl moieties, and the lower one is from the intramolecular charge transfer (ICT) transition of whole π system. **FCA** is a strong absorption chromophore with the molar extinction coefficient up to $8.97 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (ϵ_{max} at 459 nm). It is known that 9,10-bis(arylvinyl)anthracenes are weakly fluorescent and 2,6-bis(arylvinyl)anthracenes emit intensely in solutions. **FCA** shows the moderate intensity of emission with the peak wavelength of 566 nm and the fluorescence quantum yield of 12.7%, indicating that the intramolecular torsion motion of 9,10-branch still plays a role of decreasing fluorescence emission. This could be further evidenced by its broad emission band implying the existence of large amplitude relaxation in the excited state.

Fig. 1 The absorption and emission spectra of **FCA** solution in THF at $1.0 \times 10^{-5} \text{ M}$.

Fig. 2 shows the emission spectra of **FCA** in THF/water mixtures. When a large amount of water is added to the THF solution of **FCA**, the emission intensity of aqueous dispersion is gradually enhanced and reaches about three times higher than that of pure THF solution. Since water is a non-solvent for **FCA**, the dye molecules must have aggregated in THF/water mixtures with high water contents. Therefore, **FCA** is still an aggregation-enhanced emission molecule although the limited enhancement amplitude.

Fig. 2 The emission spectra of **FCA** in THF/water mixtures at 1.0×10^{-5} M.

1.3.3 Solid-state photophysical and thermal properties

FCA is an aggregation-enhanced emission dye in THF/water mixtures, which might result in strong solid-state fluorescence emission. Fig. 3 shows the absorption and emission spectra of **FCA** under pristine (as-prepared) and ground solid-states. In the pristine solid state, **FCA** has an ICT absorption band centered at 458 nm and is an orange emitting material with peak wavelength of 578 nm and fluorescence efficiency of 11.4%. In the ground solid state, the ICT absorption peak and emission spectrum, relative to the pristine solid, are red-shifted about 10 nm and 23 nm, respectively. Ground **FCA** solid emits red fluorescence with peak wavelength of 601 nm and fluorescence efficiency of 6.5%. Nevertheless, **FCA** is still fluorescent but not strong. It is known that a distorted geometry in the monomeric form (solution) limits

effective conjugation. In the solid state, however, its conjugation degree increases by stacking-induced planarization, which results in the bathochromic shift spectra. Moreover, the still partially distorted structure resulting from the internal steric hindrance of 9,10-branch, even after stacking, disturbs the close packing, to partially diminish the intermolecular quenching effects induced by planar 2,6-branch. In this context, if 2,6-branches are also designed to be distorted structure, the cruciforms with high fluorescence efficiencies could be expected.

Fig. 3 The absorption and emission spectra of **FCA** under pristine (as-prepared) and ground solid-states.

The thermal properties are investigated with thermogravimetric (TGA) and differential scanning calorimetry (DSC) analysis under nitrogen, and the TG and DSC curves of **FCA** solids are depicted in Fig. 4. TGA measurement indicates that the **FCA** has the onset decomposition temperatures around 400 °C (based on 5% weight loss), underling excellent stability. **FCA** is also stable to UV and visible light in both solution and solid state. This is different from tetravinylbenzene derivatives whose solutions were found to degrade when exposed to UV and visible light. [33] DSC experiments show that no thermal transition is detected for pristine solid before 320 °C, however, there is one endothermic transition at 148 °C followed by one broad exothermic transition centered at 187 °C for ground solid. The two thermal transitions could be ascribed to the glass transition and the followed cold-crystallization of

amorphized **FCA** solid induced by grinding. This indicates that pristine and ground **FCA** solids are in crystalline and amorphous states, respectively, and mechanical grinding could cause the changes of aggregate morphologies and spectral shifts, rendering **FCA** solid piezofluorochromism.

Fig. 4 The thermogravimetric (TGA) curve of **FCA** solid and the differential scanning calorimetric (DSC) curves of **FCA** solids under pristine (as-prepared) and ground solid-states (inset).

1.3.4 Electrochemical and Electroluminescence properties

Fig. 5 shows the cyclic voltammetry (CV) curves of **FCA** using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in acetonitrile, with silver-button working electrodes, a silver-wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. The SCE reference electrode was calibrated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard. As shown in Fig. 5, the reversible oxidative and reductive behaviors are observed and indicate that they could transport the hole and electron. The oxidative and reductive potentials are measured to be $E_{\text{ox}} = 0.38$ eV and $E_{\text{red}} = -1.87$ eV, respectively. Based on the onset oxidative and reductive potentials, the HOMO and LUMO energy levels are estimated to be -4.97 and -2.84 eV, respectively, and the corresponding band gap is calculated as 2.13 eV.

Fig. 5 The cyclic voltammetry (CV) curves of **FCA** in MeCN

While some tetra(arylvinyl)anthracene-based cruciforms have been investigated to show two-photon absorption, fluorescence sensing metal ions, piezofluorochromism, their application in electroluminescence has rarely been explored. In order to examine the EL performance, a device with the configuration of ITO/PEDOT:PSS (40 nm)/**FCA** (60 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm) has been fabricated. Fig. 6 shows the current density-luminance-voltage characteristics. The device emits red light (at 612 nm with the Commission Internationale d'Eclairage Coordinates of (0.58, 0.41), the inset in Fig. 7) with the maximal luminance of 1300 cd/cm² and the turn-on voltage of 4.2 V. The EL efficiency-voltage curve is plotted in Fig. 7. The luminous and power efficiencies are 1.31 cd/A and 0.51 lm/W, respectively. Although this EL performance itself is not impressive, [34] it is the best one among the solution-processed red fluorescent small-molecular OLEDs based on anthracene-centered cruciform molecules. It should be noted that the fluorescence efficiency of **FCA** in amorphous state is only 6.5%. This is probably the key reason for the low EL efficiency, and the better EL performances could be expected if cruciform's solid-state fluorescence efficiencies are improved. This could be achieved by introducing cyano groups to the vinyl bond of 2,6-branch to further distort the cruciform skeleton structure, which is underway in our laboratory.

Fig. 6 Current density-luminance-voltage curves of the device ITO/PEDOT:PSS (40

nm)/ **FCA** (60 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm).

Fig. 7 The luminous efficiency-power efficiency-voltage curves of the device ITO/PEDOT:PSS (40 nm)/ **FCA** (60 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm).

The inset is the electro- luminescent spectrum.

1.4 Conclusions

We have designed and synthesized a new anthracene-centered cruciform, 2,6-bis-(9,9-di(2-ethylhexyl)fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)anthracene (**FCA**). The introduction of four branched alkoxy chains makes **FCA** soluble in common organic solvents, rendering **FCA** with good film-forming capacity. **FCA** exhibits moderate aggregation-enhanced emission and piezofluorochromic properties, which could be ascribed to strongly twisted 9,10-branch. A solution-processed non-doped device affords red EL emission with the maximal luminance of 1300 cd/cm² and the luminous efficiency of 1.31 cd/A, which is the best performance among solution-processed anthracene-based materials. We believe that better EL performances could be obtained if cruciform's solid-state fluorescence efficiencies are improved by introducing cyano groups to the vinyl bond of 2,6-branch to further distort the cruciform skeleton, which is underway in our laboratory.

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437 **Scheme 1.** The structure and synthetic route of anthracene-centered cruciform (**FCA**)
438 studied in this paper.

439 **Fig. 1** The absorption and emission spectra of **FCA** solution in THF at 1.0×10^{-5} M.

440 **Fig. 2** The emission spectra of **FCA** in THF/water mixtures at 1.0×10^{-5} M.

441 **Fig. 3** The absorption and emission spectra of **FCA** under pristine (as-prepared) and
442 ground solid-states.

443 **Fig. 4** The thermogravimetric (TGA) curve of **FCA** solid and the differential scanning
444 calorimetric (DSC) curves of **FCA** solids under pristine (as-prepared) and ground
445 solid-states (inset).

446 **Fig. 5** The cyclic voltammetry (CV) curves of **FCA** in MeCN.

447 **Fig. 6** Current density-luminance-voltage curves of the device ITO/PEDOT:PSS (40
448 nm)/ **FCA** (60 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm).

449 **Fig. 7** The luminous efficiency-power efficiency-voltage curves of the device
450 ITO/PEDOT:PSS (40 nm)/ **FCA** (60 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (100 nm).

451 The inset is the electro- luminescent spectrum.

Figure R1. The CIE of device at 6 V.

Comment 3: The state of the current non-doped OLEDs based on red fluorescent dyes should be discussed in more detail and compared with your results.

Response: We agree with the reviewer's comments. We have supplied the relative references in ref. 34 to compare with our results.

Comment 4: The film quality is very important to the performance of the materials in EL devices. If technologically possible, it is better to measure the film quality. This may be helpful to understand why the EL efficiency is not so high.

Response: We agree with the reviewer's comments. We have measured the atomic force microscopy (AFM) image of the emitting material atop ITO-glass to evaluate the film quality (see the **following Figure R2**). The emitting material film is pinhole-free and quite smooth with a surface roughness (root-mean-square) of approximately 0.481 nm, and it showed that the film quality of the emitting material meet the basic requirements for solution-processed fluorescent small-molecular OLEDs.

Figure R2. 10 μm $\times$ 10 μm AFM image of spin-coated film (the emitting material deposited atop ITO-glass).

Thank you very much. Should you have any questions, please contact us without hesitate.

Sincerely yours,

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